Articles

Successful Synthesis of Polymers Containing Pendant Norbornadiene Moieties and Norbornadiene Photochemical Valence Isomerization

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ABSTRACT: Polymers (P-IIb and P-IId) containing pendant norbornadiene moieties were synthesized with a high degree of functionalization by substitution reaction of poly((chloromethyl)styrene) with potassium salts of 2,5-norbornadiene-2,3-dicarboxylic acid and 3-phenyl-2,5-norbornadiene-2-carboxylic acid, respectively, using phase transfer catalysis in DMF under mild reaction conditions. The photochemical valence isomerization of pendant norbornadiene (NBD) moiety to the quadricyclane (QC) group, which was measured by UV spectrometry, in the obtained polymers was carried out in the film state. P-IId, which contains 3-phenyl-2,5-norbornadiene moiety, showed very high photochemical reactivity upon irradiation by sunlight or high-pressure mercury lamp. Although the rate of photochemical reaction of P-IIb was lower than that of P-IId, it was found that the rate of the former polymer increased by addition of photosensitizers such as benzophenone, 4-(*N*,*N*-dimethylamino)benzophenone, and Michler's ketone. The QC groups, which were produced by irradiation with a high-pressure mercury lamp, in the polymers reverted immediately to the corresponding NBD moieties upon immersion into a (5,10,15,20-tetraphenyl-21*H*,23*H*-porphine)cobalt(II) solution of carbon tetrachloride. Furthermore, it was found that the value of heat storage for the QC group in P-IId was about 85 kJ/mol by DSC measurement of the irradiated polymer film.

Introduction

Recently, photochemical valence isomerizations between norbornadiene (NBD) derivatives and the corresponding quadricyclane (QC) derivatives have been of interest from the viewpoint of solar energy conversion and storage,[1–4] because photoenergy can be stored as strain energy in a QC molecule and then the QC molecule can release about 96 kJ/mol of thermal energy upon contact with certain catlysts or by heating. However, the NBD has a problem in the use in solar energy conversion, because the NBD molecules do not absorb visible sunlight. Also, this solar energy conversion and storage system has so far been investigated mostly on low molecular weight NBD derivatives and QC derivatives systems. Hautala et al.[1] have proposed a photosensitization valence isomerization process from the NBD to the QC with an insoluble polymeric photosensitizer containing pendant 4-(*N*,*N*-dimethylamino)benzophenone as a chromophore. Grutsch and Kutal[5] also found a effective silica-supported inorganic photosensitizer for the NBD–QC system. King and Sweet[2] reported on the reversion from the QC to the NBD using polymer-supported cobalt(II) tetraarylporphyrin catalyst. The other conventional method normally used in this system is the introduction of some chromophores into the NBD molecules. Maruyama et al.,[6–9] Mukai et al.,[10,11] and Tomioka et al.[12] reported the synthesis and photochemical valence isomerization of some NBD derivatives having carboxyl or aryl groups as chromophores to one of the two double bonds in the molecules. Yoshida et al.[13] and Yonemitsu et al.[14] also proposed synthesis and photochemical reactions of some NBD derivatives with electron donor–acceptor chromophores to both of the double bonds in the molecules, giving a high quantum yield of photoisomerization.

On the other hand, it seems that the polymer containing pendant NBD moiety could be useful as a new photoresponsive polymer in optoelectronics switch and device technology and other fields of imaging technology as well as polymeric solar energy storage systems. Recently, Kamogawa and Yamada[15] prepared photoresponsive poly(2,5-norbornadien-7-yl (meth)acrylates) by radical polymerization of the corresponding monomers; however, the rate of valence isomerization of the polymers was very slow, because this NBD moiety did not have any group causing either a red shift of absorption or improvement in photosensitivity.

Over the past several years, we have investigated[16–18] extensively phase transfer catalysis (PTC) in polymer synthesis. This method is also practical and very important for chemical modifications of polymers and syntheses of functional polymers such as photosensitive polymers[19,20] and polymeric photosensitizers[21] under mild reaction conditions.

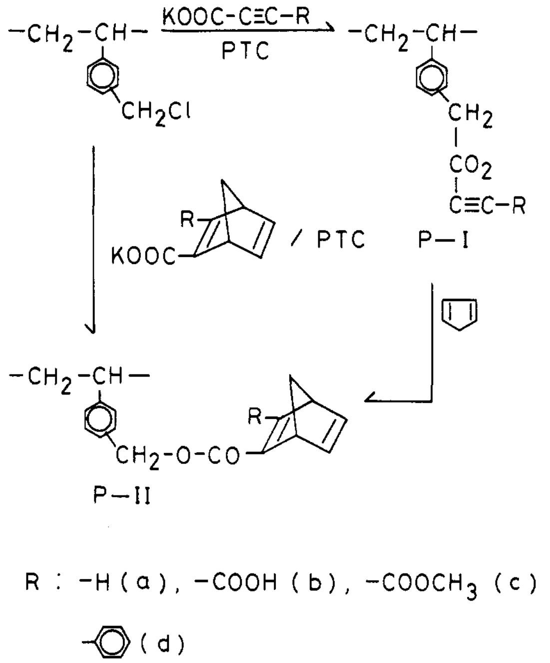
This article reports on the successful synthesis of polymers containing pendant NBD moieties by substitution reaction of poly((chloromethyl)styrene) (PCMS) with potassium salts of some NBD derivatives using PTC and investigates the photochemical valence isomerizations of the resulting polymers (Scheme I).

Experimental Section

Materials. The solvents were purified in the usual way prior to use. PCMS (the reduced viscosity of the polymer was 0.13 dL/g, measured at a concentration of 0.5 g/dL in DMF at 30 °C) and poly(2-(chloroethyl) methacrylate) (PCEMA) (the reduced viscosity was 0.69 dL/g, measured at a concentration of 0.5 g/dL in DMF at 30 °C) were prepared by radical polymerizations of (chloromethyl)styrene (mixture of 40% meta and 60% para) and 2-(chloroethyl) methacrylate using AIBN as a initiator in benzene, respectively. Poly(2-(chloroethyl) vinyl ether) (PCEVE) (the reduced viscosity was 0.62 dL/g, measured at a concentration of 0.5 g/dL in DMF at 30 °C) was synthesized by cationic polymerization of 2-(chloroethyl) vinyl ether using $BF_3{\cdot}O(C_2H_5)_2$ in toluene. Poly(epichlorohydrin) (PECH) ("HERCLOR H" from

0024-9297/89/2222-0008$01.50/0

Scheme I



Hercules Inc., reduced viscosity was 2.55 dL/g, measured at a concentration of 0.5 g/dL in DMF at 30 °C) was purified by reprecipitating it twice from THF in methanol, and then it was dried in vacuo at 50 °C. Commercial acetylenedicarboxylic acid (ADC), monopotassium salt of acetylenedicarboxylic acid (KADC), propiolic acid (PA), methyl propiolate (MPA), potassium hydroxide (KOH), methyl iodide, photosensitizers; benzophenone (BP); 4-(*N*,*N*-dimethylamino)benzophenone (DABP); Michler's ketone (MK); and a catalyst such as (5,10,15,20-tetraphenyl-21*H*,23*H*-porphine)cobalt(II) (Co-TPP) were used without further purification. Phase transfer catalyst (PTC), tetrabutylammonium bromide (TBAB) and inhibitor, and monomethoxyhydroquinone (MQ) were recrystallized from the suitable solvents, respectively. Potassium salt of 3-phenylpropiolic acid (KPPA) was prepared by the reaction of 3-phenylpropiolic acid (mp 136–137 °C) with KOH in methanol. Potassium salt of 3-carbomethoxypropiolic acid (KMPA) was prepared in 24% yield by the reaction of 10.65 g (70 mmol) of KADC with 50 mL (803 mmol) of methyl iodide using 2.55 g of TBAB at 30 °C for 24 h, followed by extraction of the resulting 3-carbomethoxypropiolic acid, reaction with KOH in methanol, and recrystallization from the mixed solvent of methanol (4)/water (1)/acetone (1). The NBD derivatives 2,5-norbornadiene-2-carboxylic acid[22] (NBCA) (mp 104–106 °C). 2,5-norbornadiene-2,3-dicarboxylic acid[23] (NDC) (mp 164–166 °C), and 3-phenyl-2,5-norbornadiene-2-carboxylic acid[24] (PNBA) (mp 125.5–126 °C) were synthesized by Diels–Alder reaction of the corresponding acetylene derivatives with cyclopentadiene as reported previously. Monopotassium salt of 2,5-norbornadiene-2,3-dicarboxylic acid (KNDC) was synthesized in 89% yield by the reaction of NDC with KOH in methanol.

Apparatus. Infrared (IR) spectra were measured on a JASCO Model A-202 spectrophotometer. UV spectra were recorded on a Shimazu Model UV-240 spectrophotometer. The ^{1}H NMR spectra were performed on a JEOL Model PS-100 spectrometer. The amount of energy storage in the pendant QC group of the polymer was measured on a Perkin-Elmer differential scanning calorimeter Model DSC System 4 at a heating rate of 3 °C/min.

Substitution Reaction of PCMS with Acetylene Derivatives Using PTC. Typical examples of the reaction are as follows.

Substitution Reaction of PCMS with PA. PCMS (0.76 g, 5 mmol) was dissolved in 10 mL of DMF, and PA (0.35 g, 5 mmol), KOH (0.28 g, 5 mmol), and TBAB (0.16 g, 0.5 mmol) as a PTC were added to the solution. The mixture was stirred at 30 °C for 24 h, and then it was poured into 500 mL of water. The obtained polymer was purified by reprecipitating it twice from THF in water and dried in vacuo at 30 °C. The yield of recovered polymer (P-Ia) was 0.70 g. The degree of substitution was 59.2 mol %, calculated from elemental analysis of chlorine (83.9 mg/g). The reduced viscosity of the polymer in DMF was 0.29 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The IR spectrum (film) showed absorption peaks at 3300 ($\equiv$CH), 2150 (C$\equiv$C), and 1710 cm^{-1} (C=O). The ^{1}H NMR spectrum ($CDCl_3$) showed signals at δ 0.9–2.4 (CH_2CH of main chain), 2.9 (CCH), 4.4 (CCH_2Cl), 5.0 (CCH_2O), and 6.1–7.5 (aromatic protons).

Diels–Alder Reaction of Cyclopentadiene with Pendant Propiolic Ester Moiety in P-Ia. The reaction of P-Ia (0.52 g, containing 1.8 mmol of propiolic ester groups) with 59.2 mol % of the ester moiety of cyclopentadiene (6 mL, 72 mmol) was carried out in THF (3 mL) at 30 °C for 24 h, and then the reaction mixture was poured into methanol. The obtained polymer was purified by reprecipitating it twice from THF in methanol and dried in vacuo at 30 °C. The yield of recovered polymer was 0.42 g. The degree of reaction was 44.1 mol %, calculated from elemental analysis of chlorine (76.2 mg/g). The IR spectrum (KBr) showed weak absorption peaks at 3300 ($\equiv$CH) and 2150 cm^{-1} (C$\equiv$C).

Substitution Reactions of PCMS with NBD Derivatives Using PTC. Typical examples of the reaction are as follows.

Substitution Reaction of PCMS with PNBA. PCMS (0.76 g, 5 mmol) and PNBA (1.06 g, 5 mmol) were reacted using KOH (0.28 g, 5 mmol) as a base and TBAB (0.16 g, 0.5 mmol) as a PTC in 10 mL of DMF at 50 °C for 72 h, and then the mixture was poured into water. The polymer obtained was purified by the same procedure as above. The yield of final polymer (P-IId) was 1.16 g. The degree of substitution was 92.9 mol %, calculated from elemental analysis of chlorine (7.9 mg/g). The reduced viscosity of the polymer in DMF was 0.18 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The IR spectrum (film) showed absorption peaks at 1690 (C=O), 1600 (C=C), and 1230 cm^{-1} (COC). The UV spectrum (film) showed the λ_{max} at 295 nm. The ^{1}H NMR spectrum ($CDCl_3$) showed signals at δ 0.9–2.3 (CH_2CH of main chain and CCH_2C), 3.8 and 4.0 (C=CCHC=C), 4.9 (CCH_2O), and 6.1–7.6 (C=CH and aromatic protons).

Typical Procedure for Photochemical Valence Isomerization of Pendant NBD Moiety in the Polymer. A solution of P-IId (0.01 g) in THF (3 mL) was cast on the inside wall of a quartz cell and dried. The polymer film on the quartz was irradiated by a 250-W high-pressure mercury lamp (Ushio Electric Co., USH-250D) without a filter at a distance of 30 cm. The rate of disappearance of the absorption peak at 295 nm was measured by a UV spectrophotometer. The sunlight irradiation of the polymer was also carried out by the same procedure.

Typical Procedure for Photosensitization Reaction of NBD Moiety in P-IIb. A solution of P-IIb and photosensitizer in THF was cast on a KBr plate and dried. The polymer film (about 2 μm) on the KBr plate was irradiated by the same 250-W high-pressure mercury lamp without a filter at a distance of 30 cm. The rate of disappearance of the absorption peak due to the C=C stretching at 1610 cm^{-1} was measured by IR spectrometry.

Measurement of Reversion from Pendant QC Group in the Polymer to the NBD Moiety. A polymer film with pendant NBD moiety was cast on the inside wall of a quartz cell and then was irradiated to produce pendant QC group in the polymer film under the same conditions. The Co-TPP solutions of carbon tetrachloride were then added to the quartz cell. The rates of increases of absorption peaks at 253 nm (P-IIb) or 295 nm (P-IId) were measured by a UV spectrometry.

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

Results and Discussion

Syntheses of the Polymers Containing Pendant NBD Moieties. Two different processes could be considered for the preparation of the polymers containing pendant NBD moieties by the reaction of PCMS using PTC (Scheme I). One is path A: the substitution reaction of PCMS with some propiolic acid derivatives followed by Diels–Alder reaction of the resulting polymer containing acetylene moieties with cyclopentadiene. The other is path

Table I
Conditions and Results of Substitution Reactions of PCMS with Propiolic Acid Derivatives

no.	PCMS, mmol	propiolic acid derivatives,[a] mmol	TBAB, mmol	DMF, mL	temp, °C	time, h	DF,[b] mol %	yield, g	η_{red},[c] dL/g
1	5	PA (5)/KOH (5)	0.5	10	30	24	59.2	0.70	0.29
2	5	KADC (5)	0.5	10	30	24	29.6	0.43	0.27
3	5	KADC (10)	0.5	10	30	24	34.9		0.30
4	5	KADC (10)	0.5	10	50	24	81.4		gel
5	5	KADC (10)[d]	0.5	10	30	48	56.0		0.23
6	5	KADC (10)[d]	0.5	10	30	72	69.7		0.24
7	5	KMPA (6)	0.5	10	30	24	7.0	0.47	0.15
8	5	KMPA (6)[e]	0.5	10	30	48	10.1		0.14
9	5	KMPA (6)[e]	0.5	10	50	24	80.0		gel
10	4	KPPA (4.8)	0.4	10	30	24	83.3	0.77	0.18

[a] PA, propiolic acid; KADC, monopotassium salt of acetylenedicarboxylic acid; KMPA, potassium salt of 3-carbomethoxypropiolic acid; KPPA, potassium salt of 3-phenylpropiolic acid. [b] Degree of functionalization. [c] Measured at a concentration of 0.5 g/dL in DMF at 30 °C. [d] 2 mmol of MQ was added as an inhibitor. [e] 0.5 mmol of MQ was added as an inhibitor.

Table II
IR and ^1H NMR Spectra of Polymers

polymer	IR spectra, cm^{-1}	^1H NMR spectra, ppm
P-Ia	3330 (≡CH), 2150 (C≡C), 1710 (C=O)	0.9–2.4 (CH_2CH of main chain), 2.9 (C=CH), 4.4 (CCH_2Cl), 5.0 (CCH_2O), 6.1–7.5 (aromatic protons)
P-Ib	3330 (≡CH), 2150 (C≡C), 1710 (C=O)	0.9–2.4 (CH_2CH of main chain), 2.9 (C=CH), 4.4 (CCH_2Cl), 5.0 (CCH_2O), 6.1–7.5 (aromatic protons)
P-Ic	3300 (≡CH), 2150 (C≡C), 1725 (C=O)	0.9–2.4 (CH_2CH of main chain), 3.7 (OCH_3), 4.4 (CCH_2Cl), 5.0 (CCH_2O), 6.1–7.4 (aromatic protons)
P-Id	2220 (C≡C), 1710 (C=O)	1.0–2.4 (CH_2CH of main chain), 4.3 (CCH_2Cl), 5.1 (CCH_2O), 6.2–7.9 (aromatic protons)
P-IIa	1730 (C=O), 1610 (C=C), 1160 (COC)	1.0–2.4 (CH_2CH of main chain and CCH_2C), 3.4 and 3.8 (C=CCHC=C), 4.4 (CCH_2Cl), 5.0 (CCH_2O), 6.0–7.4 (aromatic protons)
P-IIb	1730 (C=O), 1630 and 1610 (C=C), 1290 and 1270 (COC)	0.9–2.3 (CH_2CH of main chain and CH_2Cl), 3.6 and 3.8 (C=CCHC=C), 4.5 (CCH_2Cl), 5.0 (CCH_2O), 6.0–7.5 (C=CH and aromatic protons), 13.0 (COOH)
P-IId	1690 (C=O), 1600 (C=C), 1230 (COC)	0.9–2.3 (CH_2CH of main chain and CCH_2C), 3.8 and 4.0 (C=CCHC=C), 4.9 (CCH_2O), 6.1–7.6 (C=CH and aromatic protons)

B: the substitution reaction of PCMS with some synthesized NBD derivatives having carboxyl group under similar reaction conditions.

The former method was particularly interesting from the viewpoint of application of Diels–Alder reaction to the synthesis of a functional polymer. Substitution reactions of PCMS with some propiolic acid derivatives have been routinely performed[19] in DMF using TBAB as a PTC. As summarized in Table I, the reaction of PCMS with potassium salt of PA and KPPA gave the corresponding soluble polymers P-Ia and P-Id with 59.2 and 83.3 mol % conversions, respectively, when the reaction was carried out at 30 °C for 24 h. The IR and ^1H NMR spectra of P-Ia and P-Id are summarized in Table II.

The reaction of PCMS with KADC was carried out to synthesize the corresponding polymer (P-Ib) under the same conditions as applied to the reaction with PA. The degree of functionalization (DF) of PCMS was 29.6 mol %. Although the DF increased with increasing amounts of added KADC, with reaction temperature, or with reaction time, soluble polymer (P-Ib) with high DF did not recover when the reaction was carried out without MQ. On the other hand, the soluble polymer with 56.0–69.7 mol % conversion (this value was calculated as the P-Ib formula from the result of elemental analysis of chlorine) was obtained when the reaction was carried out in the presence of large amounts of MQ as a radical inhibitor.

Although the IR spectrum (film) of the resulting polymer showed absorptions at 3300 (≡CH stretching), 2150 (C≡C stretching), and 1710 cm^{-1} (C=O stretching), the absorption near 3400 cm^{-1} due to the carboxyl group was very weak. The ^1H NMR spectrum of this polymer showed signals of main chain protons at δ 0.9–2.4, C=CH protons at δ 2.9, CCH_2Cl protons at δ 4.4, CCH_2O protons at δ 5.0, and aromatic protons at δ 6.1–7.5. Furthermore, the intensity ratio of the proton signal of CCH at δ 2.9 was about 50% compared to that of the signals of CCH_2O at δ 5.0. This result suggests that the decarboxylation reaction of P-Ib also occurred as a side reaction. Therefore, the polymer having mainly a P-Ia formula was synthesized from the reaction of PCMS with KADC, although the substitution reaction of PCMS with KADC proceeded with relatively high DF in DMF using PTC.

The reaction of PCMS with KMPA, in which one of the carboxyl groups was esterified to protect the decarboxylation, was carried out to obtain the corresponding polymer P-Ic at 30 °C for 24 and 48 h; however, the DFs were only 7.0 and 10.1 mol %, respectively. It seems that the nucleophilicity of the carboxylate anion of KMPA was depressed by the neighboring propagyl and methyl ester groups. Although the polymer with DF = 80.0 mol % was obtained at 50 °C for 24 h in the presence of large amounts of MQ as a radical inhibitor, the recovered polymer was insoluble in any solvents. The IR and ^1H NMR spectra of P-Ic are summarized in Table II.

The Diels–Alder reaction of P-Ia having 59.2 mol % propiolic ester groups with cyclopentadiene was carried out to prepare the corresponding polymer (P-IIa) having a NBD moiety in THF at 30 °C for 24 h. The DF of this polymer was 44.1 mol % to the pendant propiolic ester group in P-Ia (calculated from the elemental analysis of chlorine); however, this polymer was insoluble in any solvents.

The reaction of P-Id having 83.3 mol % phenyl propiolic ester groups with cyclopentadiene was also carried out in boiling toluene for 24 h; however, the reaction did not proceed, and the recovered P-Id then became insoluble in any solvents.

These results mean that path A is unsuitable for the synthesis of a polymer having pendant NBD moiety.

The substitution reaction of PCMS with NBCA, which was prepared from Diels–Alder reaction of MPA with cy-

Table III
Conditions and Results of Substitution Reactions of PCMS with NBD Derivatives Having Carboxyl Group

no.	PCMS, mmol	NBD derivatives,[a] mmol	TBAB, mmol	DMF, mL	temp, °C	time, h	DF,[b] mol %	yield, g	η_{red},[c] dL/g
11	10	NBCA (10)/KOH (10)	1.0	20	30	24	80.7	1.35	0.12
12	10	KNDC (15)	1.0	20	50	4	19.0		0.16
13	10	KNDC (15)	1.0	20	50	10	29.8		0.17
14	10	KNDC (15)	1.0	20	50	24	64.2		0.17
15	10	KNDC (15)	1.0	20	50	48	78.9		0.18
16	30	KNDC (45)	3.0	60	50	72	84.4	5.93	0.22
17	5	PNBA (5)/KOH (5)	0.5	10	50	72	92.9	1.16	0.18

[a] NBCA, 2,5-norbornadiene-2-carboxylic acid; KNDC, monopotassium salt of 2,5-norbornadiene-2,3-dicarboxylic acid; PNBA, 3-phenyl-2,5-norbornadiene-2-carboxylic acid. [b] Degree of functionalization. [c] Measured at a concentration of 0.5 g/dL in DMF at 30 °C.

Table IV
Conditions and Results of Substitution Reactions of Various Polymers with KNDC

no.	polymer,[a] mmol	KNDC, mmol	TBAB, mmol	DMF, mL	temp, °C	time, h	DF,[b] mol %	yield, g	η_{red}°,[c] dL/g
18	PCEVE (10)	15	1.0	20	50	72	2.2	0.86	0.78
19	PCEMA (10)	15	1.0	20	50	72	4.6	1.42	0.76
20	PECH (10)	15	1.0	20	50	72	0.3	0.85	2.75

[a] PCEVE, poly(2-(chloroethyl)vinyl ether); PCEMA, poly(2-(chloroethyl) methacrylat); PECH, poly(epichlorohydrin). [b] Degree of functionalization. [c] Measured at a concentration of 0.5 g/dL in DMF at 30 °C.

clopentadiene, was carried out using KOH as a base and TBAB as a PTC in DMF at 30 °C for 24 h. As summarized in Table III, the DF of the polymer (P-IIa) was 80.7 mol %, which was calculated from the elemental analysis of chlorine. The IR spectrum (film) of P-IIa showed strong absorptions at 1730 (C=O stretching) and 1160 cm^{-1} (COC stretching) and a weak absorption at 1610 cm^{-1} (C=C stretching). The ^{1}H NMR spectrum of this polymer showed signals of methine protons at δ 2.7, 3.0, 3.4, and 3.8 as well as signals of main chain and CCH_2C protons at δ 1.0–2.4, CCH_2Cl protons at δ 4.4, CCH_2O protons at δ 5.0, and C=CH and aromatic protons at δ 6.0–7.4. This suggests that some pendant NBD moieties in P-IIa changed to the corresponding QC group (about 50 mol %; measured by the ^{1}H NMR spectrum) during the substitution reaction, because the CH=CH double bonds in 2-carboethoxy-2,5-norbornadiene are not thermally stable.[25]

The reaction of PCMS with 1.5 equiv of KNDC was carried out in DMF using TBAB as a PTC at 50 °C. The DF of the polymer increased with increasing reaction time, and soluble polymer (P-IIb) with DF 84.4 mol % was obtained for 72 h (Table III). The IR and ^{1}H NMR spectra of this polymer are summarized in Table II.

The reaction of PCMA with PNBA was also carried out in DMF using KOH as a base and TBAB as a PTC at 50 °C for 72 h, and soluble polymer (P-IId) with DF = 92.9 mol % was successfully synthesized in high yield. The IR and ^{1}H NMR spectra of this polymer are summarized in Table II.

These results suggested that the reactivities with KNDC and PNBA were lower than that with NBCA, because of the electron-attracting effect and steric hindrance of carboxyl and phenyl groups. However, soluble polymers (P-IIb and P-IId) containing pendant NBD moieties with high DFs were successfully synthesized by path B using TBAB as a PTC in DMF under mild reaction conditions.

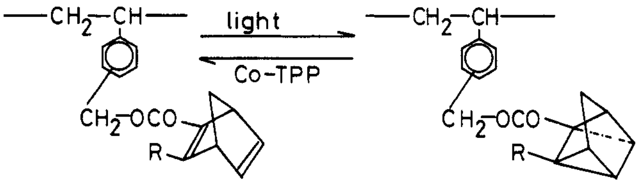
The substitution reactions of PCEVE, PCEMA, and PECH, which have pendant chloromethyl groups, with KNDC were also carried out in DMF using PTC under the same conditions as applied to the reaction of PCMS with KNDC. As summarized in Table IV, the DFs of these polymers were very low. This suggests that the reactivities of PCEVE, PCEMA, and PECH with KNDC are much lower than that of PCMS with KNDC.

Table V
Solubility of the Polymers Containing NBD Moieties

solvent	solubility of P-IIa-81	 P-IIb-84	 P-IId-93
benzene	++	+−	++
toluene	++	−	++
xylene	++	−	++
anisole	++	+−	++
hexane	−	−	−
o-dichlorobenzene	++	+−	++
carbon tetrachloride	++	−	++
chloroform	++	++	++
1,2-dichloromethane	++	+	++
acetone	++	++	+−
methyl ethyl ketone	++	++	++
ethyl acetate	++	+−	++
diglyme	++	++	++
dioxane	++	++	++
tetrahydrofuran	++	++	++
2-propanol	−	−	−
methanol	−	+−	−
NaOH–methanol soln	−	++	−
aq NaOH soln	−	+−	−

[a] ++, soluble at room temperature; +, soluble by heating; +−, partially soluble or swelling; −, insoluble.

Scheme II



As summarized in Table V, the solubility of the synthesized polymers was measured. P-IIa and P-IId were soluble in many organic solvents except hexane, methanol, and 2-propanol. On the other hand, although P-IIb, containing free carboxyl group in the NBD moiety, was soluble in NaOH–methanol solution and was slightly soluble in methanol and aqueous NaOH solution, the solubility of this polymer in organic solvents, especially in the lipophilic solvents, was lower than the solubilities of P-IIa and P-IId.

Photochemical Valence Isomerization of Pendant NBD Moiety in the Polymer. Photochemical valence isomerization between NBD derivatives and QC derivatives

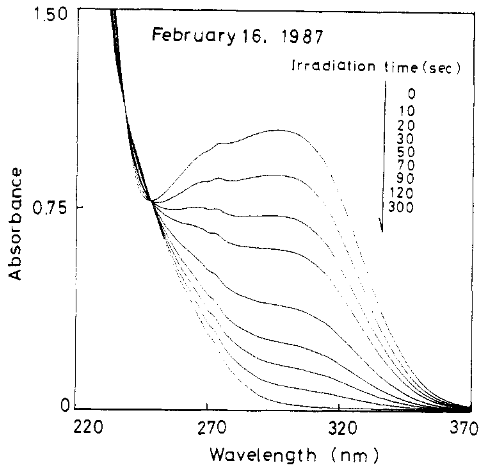


Figure 1. Change of UV spectrum of P-IId under irradiation by winter sunlight.

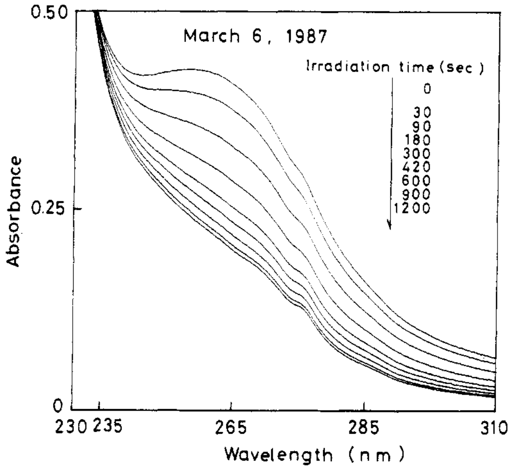


Figure 2. Change of UV spectrum of P-IIb under irradiation by winter sunlight.

by the irradiation of sunlight or UV lamp is well-known[1,6-14,26] The photochemical valence isomerization of pendant NBD moieties in P-IId and P-IIb was carried out as follows (Scheme II).

As shown in Figure 1, the film of polymer P-IId, having pendant 3-phenyl-2,5-norbornadiene moiety on the quartz cell, has very high photochemical reactivity, and the pendant NBD moiety was changed by only 5 min of solar irradiation, when this polymer was exposed to winter sunlight on February 16, 1987, on the roof of our building. In addition, this UV spectrum change showed two isosbestic points at 238 and 248 nm. This result means that the photochemical valence isomerization of pendant NBD moiety to the corresponding QC group in the polymer occurred selectively in the film state.

As shown in Figure 2, the film of P-IIb having pendant 3-carboxyl-2,5-norbornadiene moiety was also converted to the corresponding QC group by such irradiation; however, the rate of photochemical valence isomerization of this polymer was very slow.

The irradiation of polymer films of P-IId and P-IIb was also carried out by using a 250-W high-pressure mercury lamp without a filter. As shown in Figure 3, the observed rates of the photochemical reactions of the NBD moieties in the polymer films obeyed first-order kinetics, and rate constants of P-IId and P-IIb were 7.05×10^{-3} and 2.00×10^{-3}, respectively.

Furthermore, the ^{1}H NMR spectrum of P-IId measured in $CDCl_3$ showed a decrease of the signals at δ 6.8 and 7.8 due to CH=CH protons under irradiation by a high-pressure mercury lamp. This is evidence that the pendant NBD moiety of P-IId changed into the corresponding QC group with irradiation by the high-pressure mercury lamp.

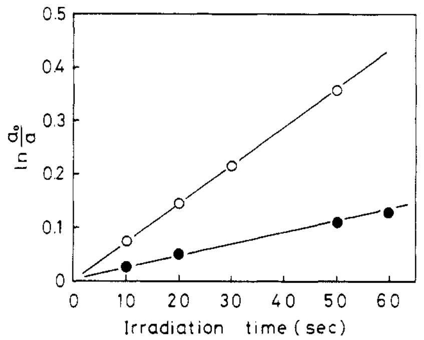


Figure 3. Rate of the reaction of NBD moieties of polymers in film state: (○) P-IId; (●) P-IIb.

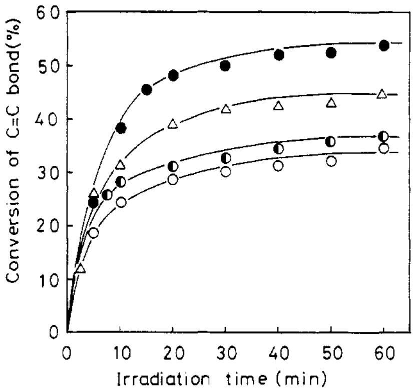


Figure 4. Rate of the reaction of NBD moiety in P-IIb in the presence of 2 mol % photosensitizer: (●) with MK; (△) with DABP; (◐) with BP; (○) with no sensitizer.

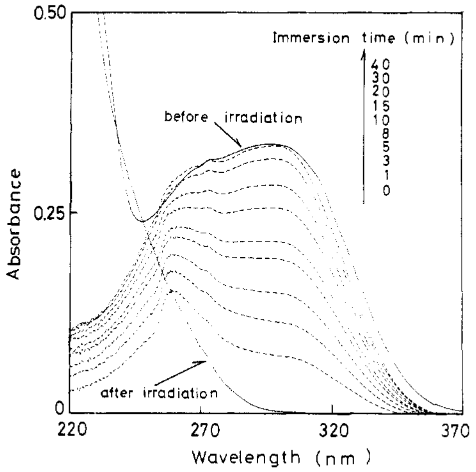


Figure 5. Change of UV spectrum of P-IId by immersion in a Co-TPP solution of carbon tetrachloride.

Since the rate of photochemical reaction of P-IIb was slower than that of P-IId, photosensitization of P-IIb was investigated. Interestingly enough, the rate of photochemical reaction of the NBD moiety in the polymer was accelerated by addition of 2 mol % of various photosensitizers such as BP, DABP, and MK, which are well-known as typical triplet photosensitizers.[27] From this result, it was found that the efficiency of these photosensitizers was as follows: MK > DABP > BP (Figure 4).

It is well-known[2-4,28,29] that QC compounds revert to the corresponding NBD compounds upon contact with Co-T-PP and other related catalysts.

As shown in Figures 5 and 6, the UV spectra of the irradiated films of P-IId and P-IIb returned immediately to the original spectrum maxima, when the irradiated films

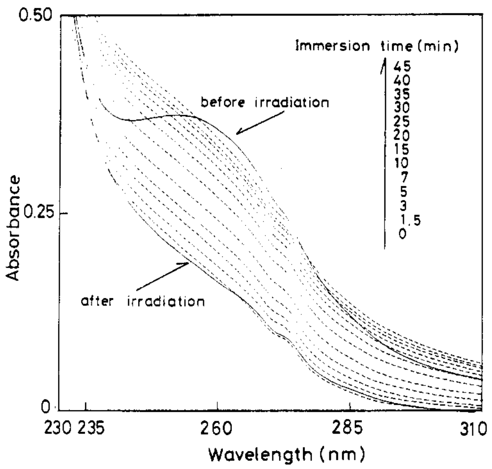


Figure 6. Change of UV spectrum of P-IIb by immersion in a Co-TPP solution of carbon tetrachloride.

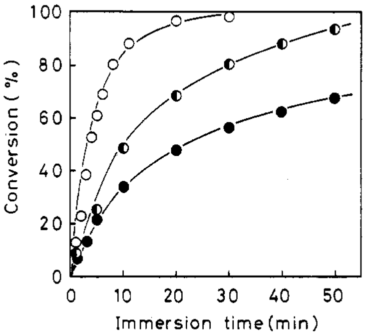


Figure 7. Rate of the reversion of pendant QC group to the corresponding NBD moiety in P-IId by immersion in various concentrations of Co-TPP–carbon tetrachloride solution: (○) at 2.4×10^{-6} g/mL; (◐) at 1.6×10^{-6} g/mL; (●) at 0.8×10^{-6} g/mL.

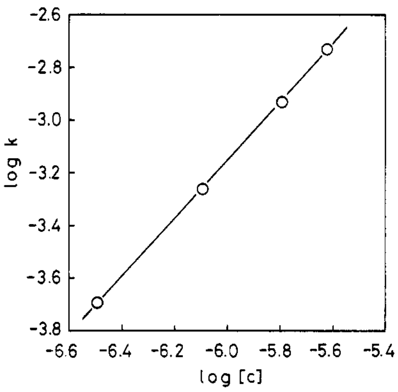


Figure 8. Correlation between the rate constant of reversion of the QC group of P-IId and Co-TPP concentration in carbon tetrachloride solution.

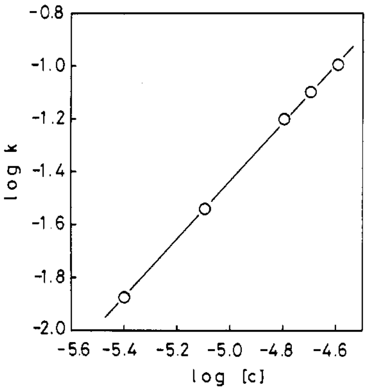


Figure 9. Correlation between the rate constant of reversion of the QC group of P-IIb and Co-TPP concentration in carbon tetrachloride solution.

of P-IId and P-IIb on the quartz cell were immersed in the solution of Co-TPP in carbon tetrachloride. This result shows that pendant QC groups in P-IId and P-IIb revert very smoothly to the corresponding NBD moieties by contact with the catalyst solution.

As shown in Figure 7, the rate of reversion of P-IId increased with increasing the Co-TPP catalyst concentration of carbon tetrachloride solution. Furthermore, it was found that the observed rates of reversion from the pendant QC group of P-IId to the corresponding NBD moiety obeyed first-order kinetics, and then the rates were linearly dependent on the catalyst concentration (Figure 8). The observed rates of reversion of P-IIb also obeyed first-order kinetics, and then the rates were linearly dependent on the catalyst concentration (Figure 9).

However, the irradiated polymer films of P-IId and P-IIb were gradually dissolved in the solution. Therefore, it seems that the above reaction rates are not real reversion rates of the pendant QC groups to the NBD moieties in the film state.

It was also confirmed that the value of heat storage for the QC group in P-IId was about 85 kJ/mol by DSC measurement of the irradiated polymer film.

Conclusions

From all these results, the following were concluded.

(1) Polymers with some pendant NBD moieties were synthesized by the substitution reaction of PCMS with potassium carboxylate of NBD compounds using phase transfer catalysis under mild reaction conditions.

(2) Pendant 3-phenyl-2,5-norbornadiene moiety in P-IId has high photochemical reactivity; furthermore, this NBD moiety converts to the corresponding QC group with high conversion by irradiation of sunlight or high-pressure mercury lamp.

(3) Although photochemical reactivity of 3-carboxyl-2,5-norbornadiene moiety in P-IIb was lower than that of P-IId, the reactivity of the former polymer was accelerated by addition of 2 mol % of various triplet state photosensitizers such as BP, DABP, and MK.

(4) The QC groups in the polymers also revert to the corresponding NBD moieties upon contact with Co-TPP catalyst solution.

(5) The QC groups of P-IId can store about 85 kJ/mol of heat energy in the molecule as strain energy.

Registry No. BP, 119-61-9; DABP, 530-44-9; MK, 90-94-8; Co-TPP, 59888-73-2; TBAB, 1643-19-2.

References and Notes

(1) Hautala, R. R.; Little, J.; Sweet, E. *Solar Energy* **1977**, *19*, 503.
(2) King, R. B.; Sweet, E. M. *J. Org. Chem.* **1979**, *44*, 385.
(3) Hautala, R. R.; King, R. B.; Kutal, C. *Solar Energy*; Hummana: Clifton, NJ, 1979.
(4) Wrighton, M. S. *Interfacial Photoprocess: Energy Conversion and Synthesis*; American Chemical Society: Washington, DC, 1980.
(5) Grutsch, P. A.; Kutal, C. *J. Chem. Soc., Chem. Commun.* **1982**, 839.
(6) Maruyama, K.; Terada, K.; Yamamoto, Y. *Chem. Lett.* **1981**, 839.
(7) Maruyama, K.; Terada, K.; Yamamoto, Y. *J. Org. Chem.* **1981**, *46*, 5294.
(8) Maruyama, K.; Tamiakim, H.; Yanai, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 781.
(9) Maruyama, K.; Tamiaki, H.; Kawabata, S. *J. Org. Chem.* **1985**, *50*, 4742.
(10) Toda, T.; Hasegawa, E.; Mukai, T.; Tsuruta, H.; Hagiwara, T.; Yoshida, T. *Chem. Lett.* **1982**, 1551.
(11) Yamashita, Y.; Hanaoka, T.; Takeda, Y.; Mukai, T. *Chem. Lett.* **1986**, 1279.

14 *Macromolecules* 1989, *22*, 14–20

(12) Tomioka, H.; Hamano, Y.; Izawa, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 821.
(13) Miki, S.; Ohno, T.; Iwasaki, H.; Yoshida, Z. *Tetrahedron Lett.* **1985**, *26*, 3487; *J. Photochem.* **1985**, *29*, 27.
(14) Hirao, K.; Ando, A.; Hamada, T.; Yonemitsu, O. *J. Chem. Soc., Chem. Commun.* **1984**, 300.
(15) Kamogawa, H.; Yamada, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1501.
(16) Nishikubo, T.; Iizawa, T.; Kobayashi, K.; Masuda, Y.; Okawara, M. *Macromolecules* **1983**, *16*, 722.
(17) Iizawa, T.; Nishikubo, T.; Masuda, Y.; Okawara, M. *Macromolecules* **1984**, *17*, 992.
(18) Iizawa, T.; Nishikubo, T.; Ichikawa, M.; Sugawara, Y.; Okawara, M. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1893.
(19) Iizawa, T.; Nishikubo, T.; Takahashi, E.; Hasegawa, M. *Makromol. Chem.* **1983**, *184*, 2297.
(20) Nishikubo, T.; Iizawa, T.; Sugawara, Y.; Shimokawa, T. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 1097.
(21) Nishikubo, T.; Uchida, J.; Matsui, K.; Iizawa, T. *Macromolecules* **1988**, *21*, 1583.
(22) Diels, O.; Alder, K. *Justus Liebigs Ann. Chem.* **1931**, *490*, 326.
(23) Mcmoy, L. *J. Am. Chem. Soc.* **1967**, *89*, 1673.
(24) Poos, G. I.; Keis, J.; Wittekind, R. R.; Rusenau, J. D. *J. Org. Chem.* **1961**, *26*, 4898.
(25) Graham, P. J.; Buhle, E. L.; Pappas, N. *J. Org. Chem.* **1961**, *26*, 4658.
(26) Leermakers, P. A.; James, F. C. *J. Org. Chem.* **1967**, *32*, 2898.
(27) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.
(28) Maruyama, K.; Tamiaki, H.; Kawabata, S. *Chem. Lett.* **1984**, 743.
(29) Maruyama, K.; Tamiaki, H. *J. Org. Chem.* **1986**, *51*, 602.

New Polymer Syntheses. 31. Poly(4-mercaptobenzoate) and Copolyester of 4-Mercaptobenzoic Acid and Various 4-Hydroxybenzoic Acids

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ABSTRACT: Poly(4-mercaptobenzoate) with $\overline{\mathrm{DP}}$s above 200 was prepared by thermal condensation of *S*-acetyl-4-mercaptobenzoic acid at temperatures in the range 300–350 °C. Poly(4-mercaptobenzoate) is highly crystalline and insoluble in all common solvents and possesses a reversible first-order solid → solid phase transition at 366 ± 2 °C as revealed by DSC and WAXS measurements. Thermogravimetric analyses show a short-time thermostability up to ca. 410 °C. Partially crystalline copolyesters were obtained by cocondensation of *S*-acetyl-4-mercaptobenzoic acid and 4-acetoxy-, 4-acetoxy-3-bromo-, 4-acetoxy-3-chloro-, and 4-acetoxy-3-methoxybenzoic acid. WAXS patterns, IR spectra, and DSC measurements indicate that these cocondensates are neither blends of homopolyesters nor block copolyesters but copolyesters with nearly random sequences. The DSC traces of copolyesters containing 4-hydroxybenzoic acid (molar ratios 3:1, 1:1, 1:3) display reversible first-order solid–solid phase transitions, at temperatures different from those of the homopolyesters. WAXS measurements conducted with synchrotron radiation at variable temperatures indicate that the high-temperature modification of the copolyesters is almost identical with that of the parent homopolyesters. Furthermore, melting points (T_m's) in the range 380–480 °C were found; yet the melting process is in all cases accompanied by thermal degradation. Thermomechanical analyses demonstrate that the heat-distortion temperatures (HDT's) of the copolyesters may be as high as or even higher than that of poly(4-mercaptobenzoate).

Introduction

From the viewpoint of chemical structure, poly(4-hydroxybenzoate), (4-Hybe)$_n$, is the ideal main-chain liquid crystal (LC) polyester. Due to the high degree of crystallinity and an extremely high (theoretical) melting point (>600 °C), it cannot be processed from the melt, because thermal degradation is too rapid at temperatures above 500 °C. In order to obtain polyesters with melting points below 400 °C the chemical structure needs to be modified in such a way that the melting enthalpy is considerably reduced and the melting entropy increased. The lattice energy, which is responsible for the melting enthalpy, is mainly based on van der Waals interactions between the aromatic rings and on the dipole moments of the ester groups. As demonstrated by Xydar,[1–3] a random sequence of monomers such as 4-Hybe, hydroquinone, 4,4′-dihydroxybiphenyl, and terephthalic acid, which prevents a regular array of dipole moments, suffices to reduce the melting point to such an extent that processing is feasible around 400 °C.

Partial and random replacement of "ether oxygens" by sulfur, i.e., random cocondensation of 4-mercaptobenzoic acid (4-Mebe) with 4-hydroxybenzoic acid (4-Hybe), might have a similar effect, because the covalent radius of the sulfur atom is significantly greater than that of oxygen. Thus, it was the purpose of the present work to study syntheses and properties of (co)polyesters containing 4-Mebe. Aromatic copolyesters containing a small percentage of 4-Mebe were claimed as thermotropic engineering plastics in a recent patent,[4] yet without any description of their properties. To the best of our knowledge poly(4-mercaptobenzoate), (4-Mebe)$_n$, and copolyesters of 4-Mebe and various 4-hydroxybenzoic acids have never been reported so far.

Experimental Section

Materials. 4-Aminobenzoic acid and 4-hydroxybenzoic acid were gifts of Bayer AG (Leverkusen, FRG) and were used without further purification. 3-Chloro- and 3-methoxy-4-hydroxybenzoic acid were purchased from Aldrich Co. (St. Louis, MO) and used without purification. 3-Bromo-4-hydroxybenzoic acid was prepared by bromination of 4-hydroxybenzoic acid in water.[5] All hydroxy acids were acetylated by means of excess acetic anhydride in boiling toluene. Marlotherm-S, a mixture of isomeric dibenzylbenzenes, was a gift of Hüls AG (Marl, FRG). It was used without further purification.

***S*-Acetyl-4-mercaptobenzoic Acid Trimethylsilyl Ester.** Crude 4-mercaptobenzoic acid was prepared from 4-aminobenzoic acid according to the procedure of ref 6 and 7. Crude 4-mercaptobenzoic acid (1.0 mol) was dissolved in a solution of 2.5 mol of potassium hydroxyde in 1.4 L of ice-water; 1.3 kg of ice and 1.25 mol of acetic anhydride were added; and the reaction mixture was shaken for 24 h at room temperature. After acidification with concentrated hydrochloric acid 0.6 mol of crude *S*-acetyl-4-mercaptobenzoic acid was isolated by filtration and dried in vacuo at 50 °C (mp 188–200 °C). This crude acid and

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