

Synthesis of polymers bearing azo-dye chromophore with photocrosslinkable moiety for nonlinear optics

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Summary

Novel photocrosslinkable second-order nonlinear optical (NLO) polymers were synthesized from radical homopolymerization of 4-[N-ethyl-N-(2-methacryloyloxyethyl)]amino-4'-(2-cinnamoyloxyethylloxycarbonyl)-2'-nitroazobenzene (MACN) or copolymerization of MACN with 2-(cinnamoyloxy)ethyl methacrylate (CM), and from polycondensation of 4-[N,N-bis(2-hydroxyethyl)]amino-4'-(2-cinnamoyloxyethylloxycarbonyl)-2'-nitroazobenzene (HACN) with p-phenylenediacryloyl chloride (PD). For the purpose of obtaining an optimized condition of UV irradiation for poling treatment involving photocrosslinking, photoreactivity of these NLO polymer films was investigated. There was observed considerably different photoreaction behavior, especially in photofading of the NLO chromophore, between MACN polymer and HACN-PD polycondensate; the latter faded more rapidly than the former. A reason for this phenomenon was considered.

Introduction

In previous paper (1), we have reported the synthesis of photocrosslinkable second-order nonlinear optical (NLO) polymers from copolymerizations of a methacrylate monomer bearing the azo-dye group as NLO chromophore with a methacrylate monomer bearing the cinnamoyl group as photoreactive moiety. Temporal stability at room temperature in second harmonic generation (SHG) of the resulted copolymer films induced by poling treatment involving photocrosslinking was found to be excellent, while it was inferior in the case of copolymer poled without photocrosslinking.

Stabilization of the poled structure might result from the fact that thermal motion of the orientated NLO chromophores was restricted by the formation of crosslinking in the copolymer. However, the restriction must be released with increase in temperature since NLO chromophore itself does not take part in crosslinking. From the view point we tried to synthesize photocrosslinkable polymers bearing the NLO chromophore with the cinnamoyl group to improve this disadvantage.

In this paper we report the synthesis of novel photocrosslinkable NLO polymers from radical homopolymerization of 4-[N-ethyl-N-(2-methacryloyloxyethyl)]amino-4'-(2-cinnamoyloxyethylloxycarbonyl)-2'-nitroazobenzene (MACN) or copolymerization of MACN with 2-(cinnamoyloxy)ethyl methacrylate (CM), and from polycondensation of 4-[N,N-bis(2-hydroxyethyl)]amino-4'-(2-cinnamoyloxyethylloxycarbonyl)-2'-nitroazobenzene (HACN) with p-phenylenediacryloyl chloride (PD). Photoreaction behavior such as photocrosslinking of the photoreactive groups and photofading of the NLO chromophores for the polymers thus prepared is also reported.

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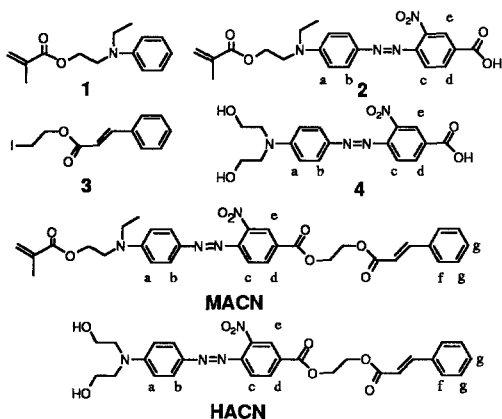
Experimental Part

Materials

Methacryloyl chloride (from Aldrich) and thionyl chloride (from Tokyo Kasei) were distilled just before use. Cinnamoyl chloride (from Tokyo Kasei) was distilled under reduced pressure just before use. N-Ethyl-N-hydroxyethyl-aniline (from Tokyo Kasei) was distilled over calcium hydride under reduced pressure. 4-Amino-3-nitrobenzoic acid (from Kodak), N,N-bis(2-hydroxyethyl)aniline, 2-iodoethanol, terephthalaldehyde and malonic acid (from Tokyo Kasei) were analytical grade and were used without further purification. 2,2'-Azobisisobutyronitrile(AIBN) as free radical initiator and dioxane, methyl ethyl ketone(MEK), diethyl ether were purified in the usual manner. All other starting materials, reagents, and solvents purchased from various chemical companies were analytical grade and were used without further purification unless otherwise noted.

Synthesis of monomers

The syntheses of MACN, HACN and their related compounds shown in Scheme I were carried out.



Scheme I Monomers(MACN and HACN) and their related compounds

N-Ethyl-N-(2-methacryloyloxyethyl)aniline (1): A mixture of N-ethyl-N-hydroxyethyl-aniline (41.3 g, 0.25 mol) and pyridine (83.3 mL) was cooled to 0 - 5°C. To the mixture methacryloyl chloride (28.2 g, 0.27 mol) in MEK (160 mL) was added dropwise in 2h while stirring. The reaction mixture was subsequently stirred for 24h at room temperature. The solution was poured into water and extracted with diethyl ether several times. The extracts were combined and the whole was washed with water and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure. The residue was distilled under reduced pressure to give an oily product. Yield: 18.7 g (32 %); bp 98°C/1 mmHg. ¹H-NMR (CDCl₃): δ 1.20 (triplet(t), 3H, J=7.2 Hz, >N-CH₂-CH₃), 1.96 (singlet(s), 3H, CH₂=C(CH₃)-CO-), 3.44 (quartet(q), J=7.6 Hz, 2H, >CH₂-CH₃), 3.62 (t, J=6.4 Hz, 2H, -O-CH₂-CH₂-N<), 4.33 (t, J=6.4 Hz, 2H, -O-CH₂-CH₂-N<), 5.59 (s, 1H, CH₂=C(CH₃)-CO-), 6.13 (s, 1H, CH₂=CH(CH₃)-CO-), 6.70 (t, J=7.2 Hz, 1H, aromatic proton), 6.75 (d, J=8.4 Hz, 2H, aromatic protons), 7.24 (multiplet(m), 2H, aromatic protons).

4-[N-Ethyl-N-(2-methacryloyloxyethyl)]amino-4'-carboxyl-2'-nitroazobenzene(2): Sodium nitrite (3.70 g, 55 mmol) was dissolved in concentrated sulfuric acid (50 mL) at 0 - 5°C. 4-Amino-3-nitrobenzoic acid (9.10 g, 50 mmol) was added to the mixture in small portions

with stirring at 0 - 5 °C to obtain diazonium salt. The reaction mixture was stirred for another 2h and poured onto cracked ice. After filtration of the mixture, an excess of remaining nitrite was decomposed by adding sodium sulfamate and pH of the mixture was adjusted to 3.5 using sodium hydroxide and sodium acetate. Solution of 1 (11.71 g, 50 mmol) in acetic acid (50 mL) was added dropwise in 30 min to the mixture at 0 - 5°C with stirring. After the addition had been completed stirring was continued overnight at 0 - 5°C. The deep red precipitate thus obtained was filtered. The filtrate was washed with water and dried under vacuum. The obtained solid was recrystallized from methanol to give compound 2. Yield: 17.10 g (44.2 %); mp 165 - 167°C. ¹H-NMR(CDCl₃): δ 1.26 (t, 3H, J=7.2 Hz, >N-CH₂-CH₃), 1.94 (s, 3H, CH₂=C(CH₃)-CO-), 3.56 (q, J=7.2 Hz, 2H, >N-CH₂-CH₃), 3.74 (t, J=6.4 Hz, 2H, -O-CH₂-CH₂-N<), 4.37 (t, J=6.4 Hz, 2H, -O-CH₂-CH₂-N<), 5.60 (s, 1H, CH₂=C(CH₃)-CO-), 6.11 (s, 1H, CH₂=C(CH₃)-CO-), 6.80 (d, J=9.6 Hz, 2H, aromatic protons a), 7.79 (d, J=9.6 Hz, 2H, aromatic protons b), 7.87 (d, J=8.8 Hz, 1H, aromatic proton c), 8.26 (d, J=8.8 Hz, 1H, aromatic proton e), 8.51 (s, 1H, aromatic proton d); the numbering of the protons is shown in Scheme I.

2-Iodoethyl cinnamate (3): A mixture of cinnamoyl chloride (18.0 g, 0.12 mol) and MEK (100 mL) was cooled to 0 - 5°C. To the mixture 2-iodoethanol (17.10 g, 0.10 mol) was added dropwise in 4h while stirring. The reaction mixture was stirred overnight at room temperature. The solution was poured into 5 wt% sodium carbonate solution and extracted with chloroform several times. The extracts were combined, washed with water and dried over anhydrous sodium sulfate. The concentrated chloroform solution was loaded onto a column of silica gel (Wako gel C-200) and purified by chromatography (chloroform), affording viscous oil. Yield: 27.23 g (90.0 %), ¹H-NMR (CDCl₃): δ 3.38 (t, J=6.8 Hz, 2H, -O-CH₂-CH₂-I), 4.47 (t, J=6.8 Hz, 2H, -O-CH₂-CH₂-I), 6.46 (d, J=16.4 Hz, 1H, -CH=CH-CO-), 7.40 (m, 3H, aromatic protons), 7.53 (m, 2H, aromatic protons), 7.74 (d, J=15.6 Hz, 1H, -CH=CH-CO-).

4-[N-Ethyl-N-(2-methacryloyloxyethyl)]amino-4'-(2-cinnamoyloxyethyl)oxycarbonyl]-2'-nitroazobenzene (MACN): To a mixture of compound 2 (8.53 g, 20 mmol), potassium carbonate (8.53 g, 20 mmol) and hexamethylphosphoramide (HMPA, 40 mL), compound 3 (6.06 g, 20 mmol) was added at room temperature and stirred for 24h (2). After completion of the reaction, the solution was poured into water containing sodium chloride and extracted with diethyl ether several times. The extracts were combined, washed with water and dried over sodium sulfate. The solvent was evaporated and the residue was purified by column chromatography (silica gel, chloroform/acetone, 15:1). After vacuum drying dark red sticky solid was obtained. Yield: 5.40 g (45.0%). ¹H-NMR (CDCl₃): δ 1.26 (t, 3H, J=7.2 Hz, >N-CH₂-CH₃), 1.94 (s, 3H, CH₂=C(CH₃)-CO-), 3.56 (q, J=7.2 Hz, 2H, >N-CH₂-CH₃), 3.74 (t, J=6.4 Hz, 2H, -O-CH₂-CH₂-N<), 4.37 (t, J=6.4 Hz, 2H, -O-CH₂-CH₂-N<), 4.59 (t, J=4.0 Hz, 2H, -O-CH₂-CH₂-O-), 4.66 (t, J=4.0 Hz, 2H, -O-CH₂-CH₂-O-), 5.60 (s, 1H, CH₂=C(CH₃)-CO-), 6.11 (s, 1H, CH₂=C(CH₃)-CO-), 6.49 (d, J=16 Hz, 1H, -CO-CH=CH-), 6.80 (d, J=9.6 Hz, 2H, aromatic protons a), 7.39 (t, J=3H, aromatic protons g), 7.54 (d, J=3.2 Hz, 2H, aromatic protons f), 7.73 (d, J=16 Hz, 1H, -CO-CH=CH-), 7.79 (d, J=9.6 Hz, 2H, aromatic protons b), 7.87 (d, J=8.8 Hz, 1H, aromatic proton c), 8.26 (d, J=8.8 Hz, 1H, aromatic proton e), 8.51 (s, 1H, aromatic proton d); the numbering of the protons is shown in Scheme I. Molecular weight. Calcd: 583. Found: 579.

2-(Cinnamoyloxy)ethyl methacrylate (CM): This monomer was the same one reported in

previous paper (1), which is shown in Scheme II.

p-Phenylenediacrylic acid: This compound was prepared according to a literature procedure (3). A mixture of terephthalaldehyde (15.83 g, 0.118 mol), malonic acid (24.70 g, 0.236 mol), piperazine (0.7 mL) and pyridine (59 mL) was stirred at 50°C for 2h and subsequently refluxed for 5h. The resulting precipitate was filtered and washed with 6N hydrochloric acid, followed by methanol to give white solid. Yield: 20.89 g (81.2 %). ¹H-NMR (DMSO-d₆): δ 6.55 (d, J=15.0 Hz, 2H, -OC-CH=CH-), 7.57 (d, J=15.0 Hz, 2H, -OC-CH=CH-), 7.69 (s, 4H, aromatic protons).

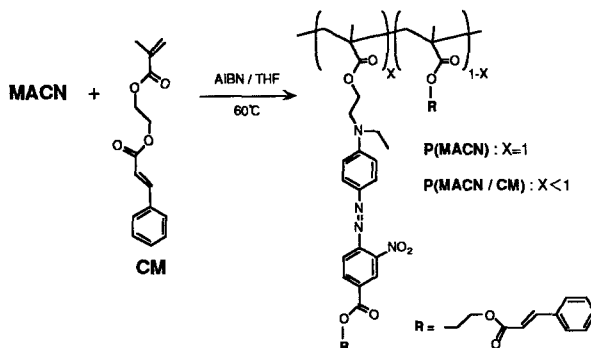
p-Phenylenediacryloyl chloride (PD): In an Ar atmosphere, *p*-phenylenediacrylic acid (3.01 g, 13.8 mmol) was refluxed with thionyl chloride (15.0 mL, 0.209 mol) and benzene (3 mL). After 1h the white solid was completely dissolved and the residual thionyl chloride was then removed by distillation, followed by vacuum pumping. The yellow solid obtained was further purified by sublimation under vacuum (4). Yield: 2.76 g (78 %). ¹H-NMR (DMSO-d₆): δ 6.62 (d, J=15.6 Hz, 2H, -OC-CH=CH-), 7.57 (d, J=16.0 Hz, 2H, -OC-CH=CH-), 7.73 (s, 4H, aromatic protons).

4-(*N,N*-Bis(2-hydroxyethyl)amino-4'-carboxyl-2'-nitroazobenzene (4): 4-Amino-3-nitrobenzoic acid (9.10 g, 50 mmol) was diazotized using sodium nitrite (3.45 g, 50 mmol) and concentrated sulfuric acid (50 mL) by almost the same procedure as described in the case of synthesis of compound 2. The pH of the reaction mixture was adjusted to 3 - 4 and solution of *N,N*-bis(2-hydroxyethyl)aniline (9.06 g, 50 mmol) in acetone (20 mL) was then added dropwise with stirring at 0 - 5°C. The mixture was further stirred overnight at 0 - 5°C and the resulted deep red precipitate was collected, and washed with water several times. Recrystallization from ethanol gave compound 4. Yield: 12.6 g (56.5 %); mp >200°C. ¹H-NMR (DMSO-d₆): δ 3.61 (s, 8H, -O-CH₂-CH₂-N), 4.89 (s, broad 2H, OH), 6.93 (d, J=9.4 Hz, 2H, aromatic protons), 7.73 (m, 3H, aromatic protons b, c), 8.20 (d, J=14.4 Hz, 1H, aromatic proton d), 8.41 (s, 1H, aromatic proton e); the numbering of the protons is shown in Scheme I.

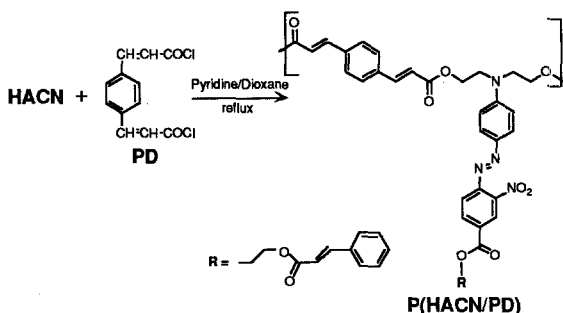
4-[*N,N*-Bis(2-hydroxyethyl)amino]-4'-(2-cinnamolyloxyethyloxycarbonyl)-2'-nitroazobenzene (HACN): This compound was synthesized using almost the same procedure as described in the case of MACN. From compound 3 (2.95 g, 7.88 mmol), compound 4 (2.38 g, 7.88 mmol), potassium carbonate (1.09 g, 7.88 mmol) and HMPA (30 mL) gave product. The product was purified by column chromatography (silica gel, acetone/*n*-hexan, 6 : 4). After vacuum drying dark red sticky solid was obtained. Yield: 1.86 g (43.1 %). ¹H-NMR (DMSO-d₆): δ 3.61 (s, 8H, -O-CH₂-CH₂-N), 4.55-4.62 (s, 4H, -CO-O-CH₂-CH₂-O-CO-), 6.72 (d, J=16.0 Hz, 1H, -O-CO-CH=CH-), 6.93 (d, J=9.2 Hz, 2H, aromatic protons a), 7.43 (m, 3H, aromatic protons g), 7.74 (m, 5H, aromatic protons b, f, and -CO-CH=CH-), 7.83 (d, J=4.8 Hz, 1H aromatic proton c), 8.25 (d, J=6.8 Hz, 1H, aromatic proton d), 8.46 (s, 1H, aromatic proton e); this numbering of the protons is show in Scheme I. Molecular weight. Calcd: 545. Found: 551.

Synthesis of polymers

The syntheses of MACN polymer, MACN-CM copolymer and HACN-PD polycondensate were carried out according to the reaction schemes shown in Scheme II and Scheme III, respectively.



Scheme II Synthesis of MACN homopolymer (P(MACN)) and MACN-CM copolymer (P(MACN / CM)).



Scheme III Synthesis of P(HACN/PD).

Homopolymer of MACN (P(MACN)) and copolymer of MACN with CM (P(MACN/CM)): Homopolymerization of MACN and copolymerization of MACN with CM were carried out under the conditions shown in Table I. In a Pyrex glass tube MACN or MACN-CM mixture and AIBN as radical initiator were dissolved in THF. The tube was cooled to liquid N₂ temperature, evacuated, filled with Ar and thawed. This procedure was repeated three times. Finally the tube was cooled to liquid N₂ temperature and sealed under vacuum. Polymerizations were performed at 60°C for 20-24h. After the polymerization, the content of the tube was poured into a large amount of methanol to precipitate the polymer. The polymer thus isolated was purified by pouring its THF solution into methanol. The purified polymers were dried under vacuum. The polymers were very soluble in chloroform and THF.

Polymer from polycondensation of HACN with PD (P(HACN/PD)): In an Ar atmosphere HACN (1.63 g, 2.98 mol) and PD (0.76 g, 2.98 mol) were dissolved in dioxane (25 mL) and pyridine (0.5 mL) was added to the solution. The mixture was heated to reflux for 2h. The resulting polymer solution was poured into a large amount of cooled ethanol. The polymer thus isolated was purified by pouring its dioxane solution into ethanol. The polymer precipitate was collected by filtration and washed with aqueous sodium bicarbonate solution, followed by water and finally rinsed with ethanol. The purified polymer was dried under vacuum. Yield: 1.86 g (77.7 %). Anal. Calcd for (C₄₀H₃₄N₄O₁₀): C, 65.75; H, 4.66; N, 7.67. Found: C, 65.09; H, 4.67, N, 7.45. The polymer is very soluble in chloroform and sparingly soluble in THF and dioxane.

Methods and measurements

Photocrosslinking of polymer films: Photocrosslinking of polymer films which were prepared by spin-coating from chloroform solutions onto quartz slides (film thicknesses were ca. 1 μm), was carried out by UV irradiation using a 500 W high-pressure mercury lamp through an optical fiber placed 4 cm above the film surface (1).

Characterization of monomers and polymers: Molecular weight measurements of monomers were performed using a Corona 117 Vapor Pressure Osmometer with chloroform as solvent. Molecular weight measurements of polymers were performed using a Tosoh HLC-8020 gel-permeation chromatograph with THF or chloroform as eluent. The columns (Tosoh TSK gel) were calibrated with polystyrene standards. Thermal analyses were performed using a Mettler TA 4000 system with a heating rate of 20°C/min. $^1\text{H-NMR}$ spectra were recorded on a JEOL EX-400 spectrometer. UV-vis spectra were obtained on a Shimadzu 3100-S UV-vis spectrometer.

Results and Discussion

Synthesis of monomers

Diazotization of 4-amino-3-nitrobenzoic acid could be conducted after dissolution in concentrated sulfuric acid. The diazotized acid successfully reacted with compound **1** to give compound **2** when the reaction was carried out by keeping pH of the reaction mixture at ca. 4. Monomer **MACN** was prepared by four reaction steps, while monomer **HACN** was prepared by two reaction steps. In these reaction steps, we attempted to react compound **3** with compound **2** or compound **4** in HMPA in the presence of potassium carbonate at room temperature. The reactions gave **MACN** and **HACN**, respectively, in a relatively high yield, which can be purified by column chromatography.

Synthesis of polymers

The initial aim of this work was to synthesize photocrosslinkable polymers bearing the NLO chromophore with the cinnamoyl group. Two types of novel photocrosslinkable NLO polymers synthesized in this report are shown in Scheme II and Scheme III, respectively.

As shown in Scheme III, **P(MACN)** was synthesized by radical polymerization of a methacrylate monomer bearing an azobenzene-type NLO moiety with photoreactive cinnamoyl group (**MACN**). **P(MACN/CM)** was synthesized by radical copolymerization of **MACN** with a methacrylate monomer bearing a cinnamoyl moiety (**CM**). Radical homopolymerization of **MACN** and copolymerization of **MACN** with **CM** were carried out using the conditions shown in Table I. The yield, NLO chromophore content, molecular weight, and glass transition temperature (T_g) of the polymers are summarized in Table II. Both homo- and copolymerization proceeded without any crosslinking reaction to give linear polymers with a relatively high molecular weight. The T_g of the polymer decreased by introducing **CM** component, which might be due to the decrease in the content of pendant rigid azobenzene moieties.

As shown in Scheme III, **P(HACN/PD)** was synthesized by polycondensation of a diol monomer bearing an azobenzene-type NLO moiety with photoreactive cinnamoyl group (**HACN**) and **PD**. The polymerization was carried out in dioxane-pyridine at refluxing temperature. The molecular weight (M_n) and T_g of **P(HACN/PD)** thus obtained were 3200 and 89.1°C, respectively. Relatively high T_g in the polymer may be attributable to that main chain of the polymer contains phenylene groups and conjugated double bonds, giving a stiffness to polymer. It is expected that **P(HACN/PD)** exhibits a higher

crosslinkability since the polymer has photocrosslinkable moieties not only in main chain but also in side chain.

Table I Conditions of radical homopolymerization of MACN and copolymerization of MACN with CM.

No.	Composition of monomer mixture (mmol)			Solvent vol. (mL)	Temp (°C)	Time (h)
	MACN	CM	AIBN			
1	3.4	—	0.164	7.82	60	20
2	3.0	7.0	0.056	23	60	24

Table II Yield, NLO chromophore content, number weight molecular weight \bar{M}_n and glass transition temperature T_g of P(MACN) and P(MACN/CM).

No.	Polymer	Yield (%)	NLO chromophore content (mol% ^a)	\bar{M}_n	T_g (°C)
1	P(MACN)	61.5	100	21000	80.6
2	P(MACN/CM)	80.1	31.4	25000	35.6

a) Determined by ¹H-NMR measurement

Photocrosslinking of polymers

For the purpose of obtaining an optimized condition of UV irradiation for poling treatment involving photocrosslinking described in previous report (1), photoreaction behavior of P(MACN), P(MACN/CM) and P(HACN/PD) was investigated.

Spectral changes in P(MACN) film caused by photocrosslinking reaction are shown in Figure 1. The absorption peaks attributable to photocrosslinkable moiety and the NLO chromophore are observed at 280 and 480 nm, respectively. Difference in the absorption spectra between P(MACN) and P(MACN/CM) was not recognized. As seen in Figure 1, decrease in the absorbance occurred at both absorption peaks upon UV irradiation, indicating that photofading of the NLO chromophores, including a cis-trans photoisomerization (4) and a photodegradation occurs other than the photocrosslinking via the 2 + 2 cycloaddition reaction of the cinnamoyl groups. The changes in the ratio of photocrosslinked cinnamoyl group and the ratio of unchanged NLO chromophore with different radiation doses at room temperature for P(MACN) and P(MACN/CM) are shown in Figure 2. The ratio of photocrosslinked cinnamoyl group was estimated by change in the absorbance at 280 nm.

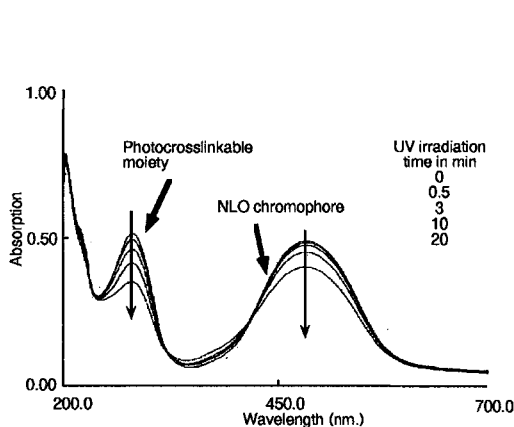


Figure 1. Spectra changes in P(MACN) film by UV irradiation

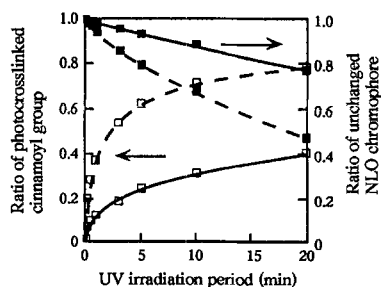


Figure 2. Changes in the ratio of photocrosslinked cinnamoyl group (□) and the ratio of unchanged NLO chromophore (■) with different radiation doses at room temperature for P(MACN) and P(MACN/CM).

(—■—) and (—□—): P(MACN)

(--■--) and (--□--): P(MACN/CM)

The ratio of unchanged NLO chromophore was expressed by the normalized absorbance at 480nm. Photocrosslinking reaction as well as photofading reaction occurred more rapidly in **P(MACN/CM)** than in **P(MACN)**. Lower T_g is considered to be favorable to accelerate photocrosslinking reaction in solid state.

Spectral changes in **P(HACN/PD)** film caused by photocrosslinking reaction are shown in Figure 3. There is observed a broad absorption band ranging from about 250nm to 370 nm and it includes a peak top at 280 nm and two shoulders at 325 and 340 nm. The peak at 280 nm appears attributable to the cinnamoyl group in side chain and the shoulders might appear attributable to the phenylenediacyrylic acid di- and mono- ester groups in main chain. The absorption peak attributable to the NLO chromophore is observed at 480 nm. As seen in Figure 3, the absorbances of these absorptions decreased upon UV irradiation. Decrease in the absorbances at 280, 325 and 340 nm implies that main chain of **P(HACN/PD)**

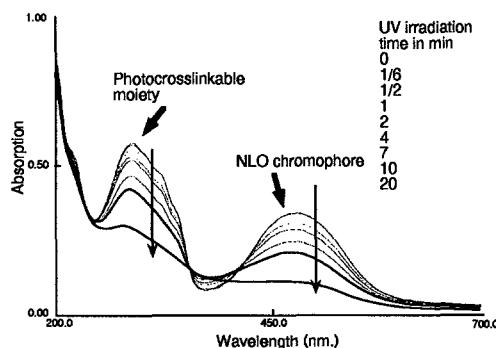


Figure 3. Spectra changes in **P(HACN/PD)** film by UV irradiation

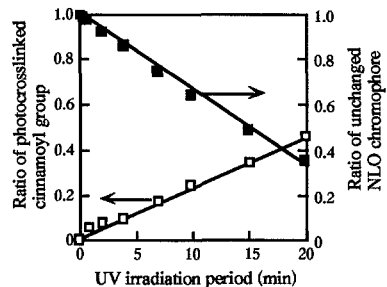


Figure 4. Changes in the ratio of photocrosslinked cinnamoyl group (□) and the ratio of unchanged NLO chromophore (■) with different radiation doses at room temperature for **P(HACN/PD)**

participates photocrosslinking (4) other than the cinnamoyl group in side chain. The changes in the ratio of photocrosslinked cinnamoyl group and the ratio of unchanged NLO chromophore with different radiation doses at room temperature for **P(HACN/PD)** are demonstrated in Figure 4. The ratios were estimated from changes in the absorbances at 280 and 480 nm, respectively. From Figure 4 it is apparent that more than 60 % of NLO chromophore already faded in 20 min. The fading speed is much faster than the case of **P(MACN)**. This behavior might be caused by the following reason. In **P(HACN/PD)** the NLO chromophores as side chains are connected along main chain in less packed state, thereby inducing cis-trans photoisomerization of the NLO chromophores rather easier as compared with **P(MACN)**.

Studies on NLO properties of these polymer films induced by poling treatment involving photocrosslinking are now under way. The results will be reported elsewhere.

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