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Study of Photopolymers. 26. Novel Synthesis of Self-Sensitized Photosensitive Polymers by Addition Reactions of Poly(glycidyl methacrylate) with Nitroaryl Cinnamate

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ABSTRACT: The additions of 4-nitrophenyl cinnamate (NPC) and 4-nitro-1-naphthyl cinnamate (NNC) to the pendant epoxide groups of poly(glycidyl methacrylate) (PGMA) and its methyl methacrylate copolymer (coPGMA) using quaternary salts as catalyst were carried out to obtain self-sensitized photosensitive polymers as shown in Scheme I. The reactions of pendant epoxide groups in coPGMA with NPC and NNC were affected by the nature of the solvent, the catalyst, and the phenoxide of the ester and proceeded to high conversions without production of any gel compound in *N*-methyl-2-pyrrolidone, diglyme, cyclohexanone, dioxane, and sulfolane at 90–130 °C using quaternary salts containing Cl^-, Br^-, or I^- as counterions. Also the reaction of PGMA, prepared by radical polymerization of glycidyl methacrylate, with NPC proceeded quantitatively in a one-pot system using diglyme or dioxane at 100 °C for 24 h. The rates of photochemical reaction of the obtained polymers having two complementary functional groups, such as the cinnamic ester moiety and a photosensitizer, were measured by IR spectrometry. The rate of photochemical reaction of these polymers was highly dependent on the degree of their functionalization. Photoreactions of polymers containing much pendant 4-nitrophenoxide as photosensitizer were faster than those of similar polymers containing 4-nitro-1-naphthoxide; interestingly, however, the latter polymers showed higher practical photosensitivity, as measured by the gray-scale method.

Introduction

Addition reactions of alcohols, phenols, carboxylic acids, and amines to pendant epoxide groups in poly(glycidyl methacrylate) (PGMA) and its copolymers are well-known.[1-6] Therefore, PGMA and its copolymers have been widely used as starting polymers for the syntheses of functional polymers and cross-linkable polymers.[7] We have reported[8] the syntheses of photosensitive polymers containing pendant photosensitive moieties by addition reaction of pendant epoxide groups in the polymer with photoreactive carboxylic acids such as cinnamic acid and methacrylic acid: However, β-hydroxyl groups in the resulting polymers conferred undesirable solubility and reactivity properties. Formation of free hydroxyl groups is avoided in reactions of epoxy compounds with acid chlorides[9] and esters;[10] syntheses of polyesters by the addition reactions of bisepoxide with dicarboxylic acid chlorides[11] or the esters[12] have been reported. However, the syntheses of functional polymers by addition reactions of pendant epoxide groups of PGMA and its copolymers with acid chlorides or esters have not been reported before our recent publications.[13,14].

The article reports on the syntheses of self-sensitized photosensitive polymers containing both pendant cinnamic ester and suitable photosensitizer groups and discusses the photochemical reactions of the obtained polymers.

Experimental Section

Materials. The solvents were purified in the usual way prior to use. Azobis(isobutyronitrile) (AIBN) was recrystallized twice from methanol at 40 °C. Glycidyl methacrylate (GMA) and methyl methacrylate (MMA) were distilled twice under reduced pressure. Reaction of 4-nitrophenol and cinnamoyl chloride in THF using pyridine as HCl acceptor according to the reported method[15] followed by two recrystallizations from methanol gave 4-nitrophenyl cinnamate (NPC) (mp 145–146 °C). 4-Nitro-1-naphthyl cinnamate (NNC) was similarly synthesized and purified in 89.7% yield from 4-nitro-1-naphthol and cinnamoyl chloride (mp 149–150 °C). Anal. Calcd for $C_{19}H_{13}NO_4$: C, 71.47; H, 4.10; N, 4.39. Found: C, 71.56; H, 4.10; N, 4.35.

Other esters such as phenyl benzoate (PB) (mp 67–68 °C), 4-nitrophenyl benzoate (NPB) (mp 142–143 °C), 4-chlorophenyl benzoate (CPB) (mp 86–87 °C), and 4-methoxyphenyl benzoate (MPB) (mp 88–89 °C) were obtained quantitatively by the reactions of benzoyl chloride with the corresponding phenols by the same method. Reagent-grade triethylamine (TEA), tetramethylammonium bromide (TMAB), tetraethylammonium bromide (TEAB), tetraethylammonium chloride (TEAC), tetra-*n*-propylammonium bromide (TPAB), tetra-*n*-butylammonium bromide (TBAB), tetra-*n*-butylammonium iodide (TBAI), tetra-*n*-butylammonium hydrogen sulfate (TBAH), tetra-*n*-butylammonium perchlorate (TBAP), tetra-*n*-butylphosphonium bromide (TBPB), and benzoic acid were used without further purification. Poly(glycidyl methacrylate-*co*-methyl methacrylate) (coPGMA) was prepared in 90% yield by radical copolymerization of GMA (30 g, 0.21 mol) and MMA (20 g, 0.20 mol) using AIBN (0.3 g) as an initiator in benzene at 60 °C for 3 h and then 80 °C for 2 h under flowing nitrogen, followed by one precipitation in *n*-hexane, two precipitations from THF into *n*-hexane, and drying at 50 °C under reduced pressure. The epoxide equivalent, which was measured by the HCl–pyridine method according to the reported method,[16] of the obtained polymer was 251. The reduced viscosity of the polymer in DMF was 0.23 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. Poly[2-(cinnamoyloxy)-3-chloropropyl methacrylate-*co*-methyl methacrylate] (coPCCPMA) containing 99.0 mol % pendant cinnamic ester moiety was synthesized by the reaction of coPGMA with cinnamoyl chloride according to the reported method.[13]

Typical Procedure for the Addition Reaction of coPGMA with NPC. coPGMA (1.00 g, 4 mmol) was dissolved in 10 mL of sulfolane, and NPC (1.08 g, 4 mmol) and TEAC (0.066 g, 0.4 mmol) were added to the solution. The mixture was stirred at 130 °C for 24 h, and then it was poured into ethanol (200 mL). The obtained polymer was purified by reprecipitating twice from THF into methanol and finally dried in vacuo at 50 °C. The yield of the recovered polymer was 1.68 g. The degree of addition reaction of pendant epoxide group in the polymer, calculated from the elemental analysis of nitrogen and the intensity of the ^1H NMR spectrum, was 95.1 mol %. The reduced viscosity of the polymer in DMF was 0.21 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The IR spectrum (film) showed absorption peaks at 1720 (C═O stretching), 1640 (C═C stretching of cinnamic ester), and 1520 and 1340 cm^{-1} (NO_2 stretching). The ^1H NMR spectrum ($CDCl_3$) showed signals at δ 0.95 (CCH_3), 1.90 (CCH_2C), 3.50 (OCH_3), 4.30 (OCH_2C), 5.50 (OCHC), 6.40 and 7.70 (CH═CH, doublet), and 6.95–8.20 (aromatic protons of cinnamate and 4-nitrophenoxide).

Typical Procedure for the Addition Reaction of coPGMA with NNC. The reaction of coPGMA (1.00 g, 4 mmol) with NNC

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(1.28 g, 4 mmol) was carried out in the presence of TEAC (0.066 g, 0.4 mmol) in sulfolane (10 mL) at 130 °C for 24 h and the reaction product was purified by the procedure described above. The yield of the final polymer was 1.55 g. The degree of addition reaction of pendant epoxide group in the polymer was 83.5 mol %, calculated from the elemental analysis of nitrogen. The reduced viscosity of the polymer in DMF was 0.30 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The IR spectrum (film) showed absorption peaks at 1720 (C=O stretching), 1640 (C=C stretching of cinnamic ester), and 1520 and 1330 cm^{-1} (NO_2 stretching). The ^{1}H NMR spectrum showed signals at δ 0.95 (CCH_3), 1.90 (CCH_2C), 3.50 (OCH_3), 4.40 (OCH_2C), 5.50 (OCHC), and 6.40–8.60 (aromatic protons of cinnamate and 4-nitro-1-naphthoxide).

Typical Procedure for Synthesis of Self-Sensitized Photosensitive Polymer Containing Pendant Cinnamic Ester and Photosensitizer Groups in a One-Pot System. GMA (4.37 g, 30 mmol) and AIBN (0.043 g, 0.26 mmol) were dissolved in dioxane (15 mL), and the polymerization was carried out at 60 °C for 5 h and then at 80 °C for 2 h under flowing nitrogen. After the polymerization was complete, a few grains of hydroquinone monomethyl ether, NPC (8.10 g, 30 mmol), and TEAB (0.63 g, 3 mmol) dissolved in dioxane (50 mL) were added at room temperature. The mixture was stirred at 100 °C for 24 h, poured into ethanol (500 mL), reprecipitated twice from THF into methanol, filtered, and dried in vacuo at 50 °C. The yield of the obtained polymer was 9.88 g. The degree of addition reaction of pendant epoxide group in the polymer with NPC, calculated from the elemental analysis of nitrogen and the intensity of the ^{1}H NMR spectrum, was 97.5 mol %. The reduced viscosity of the polymer in DMF was 0.32 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The IR spectrum (film) showed absorption peaks at 1720 (C=O stretching), 1640 (C=C stretching of cinnamic ester), and 1520 and 1340 cm^{-1} (NO_2 stretching). The ^{1}H NMR spectrum ($CDCl_3$) showed signals at δ 1.00 (CCH_3), 1.90 (CCH_2C), 4.30 (OCH_2C), 5.50 (CCHC), 6.40 and 7.70 (CH=CH, doublet), and 6.95–8.20 (aromatic protons of cinnamate and 4-nitrophenoxide).

Measurement of Photochemical Reaction of the Polymer. The polymer solution in THF was cast on a KRS (composition: ThCl + ThBr) plate and dried. The polymer film (about 5 μm) on the plate was irradiated by a 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 due to the C=C group at 1640 cm^{-1} was measured by IR spectrometry (JASCO Model A-202).

Measurement of Practical Photosensitivity of the Polymer. The photosensitivity of the polymer was measured by the gray-scale method[17] as follows: the polymer (0.2 g) was dissolved in cyclohexanone (2 mL), and then it was cast on a copper plate by using a rotary applicator and dried. A Kodak step tablet no. 2 (Eastman Kodak Co.) was placed upon this film, and then it was exposed by a photochemical lamp (Mitsubishi Electric Co., FL15SBL-360) (15 W × 7) for 3 min at a distance of 3 cm. The exposed film on the plate was developed in ethyl acetate for 2 min, and the photosensitivty was determined from the remaining step number.

Results and Discussion

Addition Reaction of Pendant Epoxide Group in the Polymer with Ester. Addition reactions of coPGMA with NPC proceeded with 45–68 mol % conversions using TEAC as a catalyst in *N*-methyl-2-pyrrolidone (NMP), diglyme, dioxane, cyclohexanone, and sulfolane at 90 °C for 24 h. Under these conditions, it was found that NMP, diglyme, and cyclohexanone were better than dioxane and sulfolane as the reaction solvent. However, the degree of conversion of the reaction of coPGMA with NPC increased with temperature in sulfolane, where the reaction eventually gave the corresponding polymer with quantitative conversions at 120–130 °C without any gel products (Table I).

The reaction of coPGMA with NNC also gave the corresponding polymer product with 35–52 mol % conversions in the same solvents at 90 °C for 24 h, and the degree of conversion also increased with temperature in sulfolane. However, the degrees of conversions of the reaction of coPGMA with NNC were generally lower than those of the reaction of coPGMA with NPC under the same reaction conditions. This suggests that the reactivity of NNC to pendant epoxide groups in coPGMA was lower than that of NPC under the same reaction conditions when TEAC was used as a catalyst.

Table I
Conditions and Results of Addition Reactions of coPGMA with Cinnamic Esters[a]

no.	solvent	ester	*T*, °C	DF, mol %	yield, g	η_{red},[b] dL/g
1	NMP[c]	NPC	90	67.9	1.21	0.22
2	diglyme	NPC	90	66.3	1.46	0.23
3	cyclohexanone	NPC	90	62.0	1.42	0.24
4	dioxane	NPC	90	45.2	1.38	0.23
5	sulfolane	NPC	90	49.5	1.31	0.23
6	sulfolane	NPC	100	59.6	1.43	0.23
7	sulfolane	NPC	110	73.8	1.57	0.22
8	sulfolane	NPC	120	93.9	1.66	0.20
9	sulfolane	NPC	130	95.1	1.68	0.21
10	diglyme	NNC	90	51.9	1.39	0.19
11	cyclohexanone	NNC	90	45.4	1.13	0.23
12	dioxane	NNC	90	36.3	1.13	0.22
13	sulfolane	NNC	90	35.7	1.31	0.31
14	sulfolane	NNC	100	53.7	1.53	0.32
15	sulfolane	NNC	110	71.9	1.44	0.30
16	sulfolane	NNC	120	83.4	1.52	0.30
17	sulfolane	NNC	130	83.5	1.55	0.30

[a] Each reaction was carried out with 4 mmol of coPGMA and 4 mmol of cinnamic ester using 0.4 mmol of TEAC as a catalyst in 10 mL of the solvent for 24 h. [b] Measured at a concentration of 0.5 g/dL in DMF at 30 °C. [c] *N*-Methyl-2-pyrrolidone.

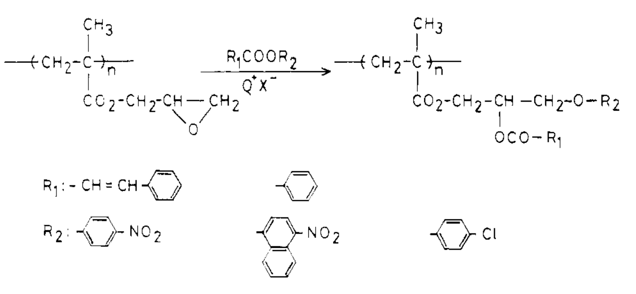
Table II
Catalyst Effect on Addition Reactions of coPGMA with Cinnamic Esters[a]

no.	catalyst	ester	DF, mol %	yield, g	η_{red},[b] dL/g
18	none	NPC	12.9	0.89	gel
19	TEA	NPC	71.4	0.87	0.52
20	TMAB	NPC	85.5	1.67	0.20
21	TEAB	NPC	93.7	1.67	0.20
22	TPAB	NPC	92.8	1.54	0.20
23	TBAB	NPC	86.0	1.67	0.18
24	TBAI	NPC	84.6	1.43	0.19
25	TBAH	NPC	4.5	0.89	gel
26	TBAP	NPC	24.7	0.95	gel
27	TBPB	NPC	89.0	1.62	0.18
28	none	NNC	31.7	1.14	gel
29	TEA	NNC	34.4	0.89	6.31
30	TEAB	NNC	70.5	1.46	0.33

[a] Each reaction was carried out with 4 mmol of coPGMA and 4 mmol of cinnamic ester using 0.4 mmol of the catalyst in 10 mL of sulfolane at 100 °C. [b] Measured at a concentration of 0.5 g/dL in DMF at 30 °C.

Although the reactions of coPGMA with NPC and NNC proceeded with 12.9 and 31.7 mol % conversions, respectively, without any catalyst in sulfolane at 100 °C for 24 h, the obtained products were gel compounds. The reactions of coPGMA with NPC and NNC produced the corresponding polymers with relatively high conversions of 71.4 and 34.4 mol %, respectively, in sulfolane at 100 °C for 24 h when TEAC was employed as a catalyst. However, the viscosities of the obtained polymers were abnormally high. It seems that some side reaction such as ring-opening polymerization of pendant epoxide groups occurred during the addition reactions of the epoxide groups of coPGMA with NPC and NNC when TEA was used as a catalyst (Table II).

Scheme I



The reactions of coPGMA with NPC and NNC were significantly facilitated by the addition of catalytic amounts of the other quaternary salts TMAB, TEAB, TPAB, TBAB, TBAI, and TBPB, without abnormally increasing the viscosity of the product polymers. However, the reactions of coPGMA with NPC using TBAH and TBAP in sulfolane at 100 °C for 24 h occurred with only 4.5 and 24.7 mol % conversions, respectively, to give gel products.

These results mean that quaternary salts containing Cl^-, Br^-, or I^- as counterions are excellent catalysts for addition reactions of pendant epoxide groups with cinnamic esters. On the other hand, quaternary salts with HSO_4^- or ClO_4^- as counterions and tertiary amines such as TEA are poor catalysts for these reactions.

The IR spectrum (film) of the polymer obtained from the reaction of coPGMA with NPC showed absorptions at 1720 (C=O stretching), 1640 (C=C stretching), and 1520 and 1340 cm^{-1} (NO_2 stretching) but showed no absorption due to OH stretching near 3500 cm^{-1} and the disappearance of the absorption due to the epoxide ring at 905 cm^{-1}. The ^1H NMR spectra of this polymer showed signals of CCH_3 protons at δ 0.95, CCH_2C protons of the main chain at δ 1.90, OCH_3 protons at δ 3.50, OCH_2C protons at δ 4.30, O-CH-C proton at δ 5.50, CH=CH protons at δ 6.40 (doublet) and 7.70 (doublet), and aromatic protons of cinnamate and 4-nitrophenoxide at δ 6.95–8.20. In addition, the degree of the reaction of pendant epoxide groups in coPGMA with NPC calculated from the intensity ratio of the ^1H NMR spectrum was consistent with the value obtained from elemental analysis.

The polymer synthesized by the addition reaction of coPGMA with NNC showed the correct IR and ^1H NMR spectra, and the intensity ratios of the ^1H NMR spectrum of this polymer corresponded very well with the results of the elemental analysis. Recently, Funahashi[10] reported the selective synthesis of 1-methyl-2-phenoxyethyl acetate by the reaction of methyloxirane with phenyl acetate using basic catalysis.

These results suggest that poly[2-(cinnamoyloxy)-3-(4-nitrophenoxy)propyl methacrylate-*co*-methyl methacrylate] (coPCNPMA) and poly[2-(cinnamoyloxy)-3-(4-nitro-1-naphthoxy)propyl methacrylate-*co*-methyl methacrylate] (coPCNNMA), each having the same pendant photosensitive cinnamic ester moiety but a different photosensitizing group, can be prepared without side reactions by the respective addition reactions of coPGMA with NPC and NNC, using the quaternary salts TMAB, TEAB, TEAC, TPAB, TBAB, and TBPB as catalysts at 90–130 °C (Scheme I).

To explore the reactivity of esters with pendant epoxide groups in coPGMA, the reactions of coPGMA with several benzoic esters were carried out in sulfolane using TBAB as a catalyst at 100 °C for 24 h. The reactions of coPGMA with MPB and PB proceeded with only 2.6 and 8.7 mol % conversions, respectively. On the other hand, the reactions of coPGMA with NPB and CPB gave the corresponding polymers with 89.4 and 71.8 mol % conversions, respectively. This suggests that electron-attracting substituents on the ester increase its reactivity toward epoxide groups, while electron-donating substituents have the opposite effect (Table III).

Table III
Conditions and Results of Addition Reactions of Pendant Epoxide Groups in Polymers with Various Esters[a]

no.	polymer (mmol)	ester (mmol)	solvent (mL)	DF, mol %	yield, g	η_{red},[b] dL/g
31	coPGMA (4.0)	MPB (4.0)	sulfolane (10)	2.6	0.79	
32	coPGMA (4.0)	PB (4.0)	sulfolane (10)	8.7	0.80	
33	coPGMA (4.0)	CPB (4.0)	sulfolane (10)	71.8	1.32	
34	coPGMA (4.0)	NPB (4.0)	sulfolane (10)	89.4	1.30	
35	PGMA (30.0)	NPC (30.0)	diglyme (65)	99.2[c]	9.27	0.45
36	PGMA (3.0)	NPC (30.0)	dioxane (65)	97.5[c]	9.88	0.32
37	PGMA (30.0)	NNC (30.0)	diglyme (65)	56.3[c,d]	6.68	6.00
38	PGMA (30.0)	NNC (30.0)	diglyme (65)	c		gel

[a] Each reaction was carried out using 10 mol % TBAB as a catalyst at 100 °C for 24 h. [b] Measured at a concentration of 0.5 g/dL in DMF at 30 °C. [c] 10 mol % TEAB was used. [d] The reaction was carried out for 10 h.

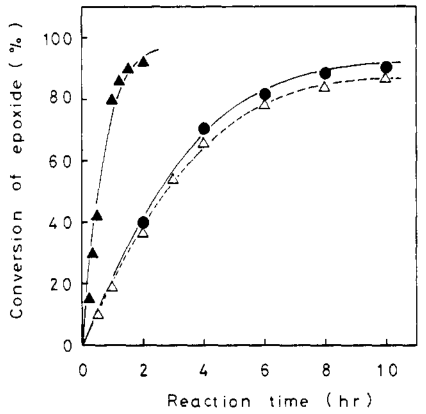


Figure 1. Addition reactions of coPGMA with NPB and benzoic acid in sulfolane using TBAB as a catalyst. The reaction of coPGMA (40 mmol) with NPB or benzoic acid (40 mmol) was carried out in sulfolane (100 mL) using TBAB (4 mmol): (▲) with benzoic acid at 100 °C; (●) with NPC at 100 °C; (△) with benzoic acid at 80 °C.

As shown in Figure 1, the reactivity of NPB toward pendant epoxide groups in coPGMA was also compared with that benzoic acid, using TBAB as a catalyst in sulfolane. The rate of reaction with benzoic acid at 100 °C was higher than with NPB at the same temperature. However, the rate of reaction with benzoic acid at 80 °C was slightly lower than with NPB at 100 °C.

The one-pot reaction for the synthesis of poly[2-(cinnamoyloxy)-3-(4-nitrophenoxy)propyl methacrylate] (PCNPMA) was carried out by radical polymerization of GMA using AIBN as an initiator at 60 °C for 5 h and then 80 °C for 2 h, followed by the addition reaction of the produced polymer (PGMA) with NPC using TEAB as a catalyst in dioxane and diglyme at 100 °C for 24 h. This reaction proceeded quantitatively to produce PCNPMA without any gel product (Table III). This reaction of PGMA with NNC was also investigated in a one-pot system under the same reaction conditions. Poly[glycidyl methacrylate-*co*-2-(cinnamoyloxy)-3-(4-nitro-1-naphth-

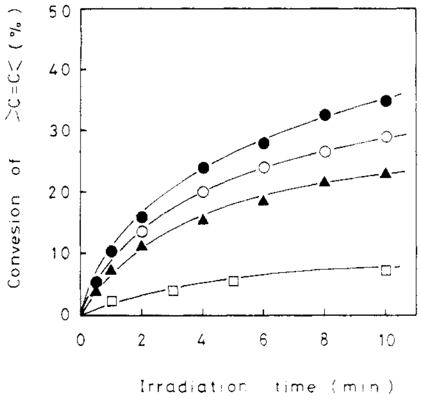


Figure 2. rate of disappearance of the CH═CH group (cinnamic ester moiety) during irradiation with a high-pressure mercury lamp: (□) coPCCPMA containing 99.0 mol % pendant cinnamic ester group; (▲) coPCNNMA containing 71.9 mol % of two pendant functional groups; (○) PCNPMA containing 97.5 mol % of two pendant functional groups; (●) coPCNPMA containing 73.8 mol % of two pendant functional groups.

oxy)propyl methacrylate] containing 56 mol % each of pendant photosensitive and photosensitizer groups was obtained 100 °C after 10 h but was accompanied by an abnormal increase of the viscosity of the polymer product. Prolonged reaction time of PGMA with NNC (24 h for 100 °C) produced gel compounds. It seems that polymer highly functionalized with cinnamic ester and 4-nitro-1-naphthoxy groups is relatively unstable at elevated temperatures.

From all these results, it was concluded that the reactions of pendant epoxide groups with esters are an excellent method for the syntheses of polymers with two different functional groups, such as a photosensitive moiety and its photosensitizing group.

Photochemical Reaction of the Obtained Polymer. The photochemical reactions of the product polymers were carried out under identical conditions by irradiation with UV light of a polymer film on a KRS plate. The rate of disappearance of the C═C bond (in the cinnamic ester moiety in the polymer) was measured by IR spectrometry. As shown in Figure 2, the rates of disappearance of the C═C bonds in coPCNPMA containing 74 mol % cinnamic ester and 4-nitrophenoxide groups and in coPCNNMA containing 72 mol % cinnamic ester and 4-nitro-1-naphthoxide groups were much higher than that of coPCCPMA, which had 99.0 mol % cinnamic ester and chloromethyl groups.[13] However, the photochemical reaction of the cinnamic ester moiety in coPCNNMA was slower than that in coPCNPMA. Furthermore, the rate of photoreaction of PCNPMA containing 97.5 mol % of the two functional groups (synthesized by the reaction of homopolymer of GMA with NPC in a one-pot reaction system) was lower than that of coPCNPMA containing 74 mol % of the two functional groups. This suggests that self-sensitized photosensitive polymers such as PCNPMA, coPCNPMA, and coPCNNMA have high photochemical reactivity, though the rate of photochemical reaction depends on the degree of functionalization (DF) of the polymer.

The effects of the degrees of functionalization in coPCNPMA and coPCNNMA on conversions of the C═C bond after 10-min irradiation are shown in Figure 3. coPCNPMA and coPCNNMA are most photoreactive at about DF 70 and 50 mol%, respectively. In addition, it was found that the rates of photoreaction of coPCNPMA were much higher than those of coPCNNMA when their degrees of functionalization were higher than about 50 mol %.

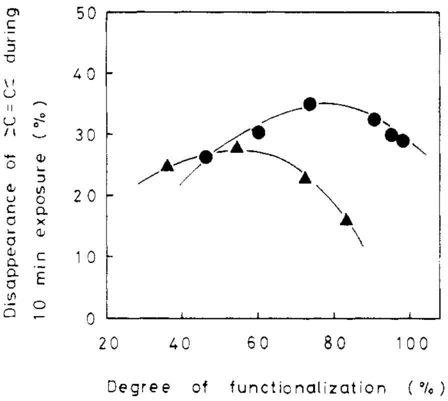


Figure 3. Relation between the content of two functional groups in the polymer and conversions of the CH═CH group (cinnamic ester moiety) by 10 min of irradiation: (●) coPCNPMA; (▲) coPCNNMA.

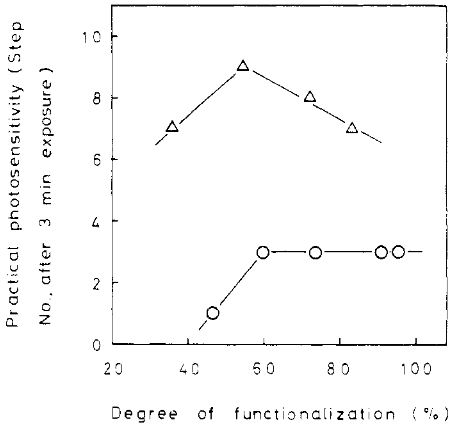


Figure 4. Relation between the content of two functional groups in the polymer and practical photosensitivity: (○) coPCNPMA; (▲) coPCNNMA.

Recently, Nishikubo et al. reported[18,19] that other self-sensitized photosensitive polymers containing the cinnamic ester moiety and varying quantities of 4-nitrophenoxide or 4-nitro-1-naphthoxide groups are most photoreactive at only about DF 30 or 15 mol % respective photosensitizer. Thus, the coPCNPMA and coPCNNMA polymers here described contain up to 75 or 80 mol % surplus photosensitizer, which, by nonproductive absorption of part of the incident UV, in fact decreases the photoreactivity of the total polymer film.[20]

Practical photosensitivities of the obtained polymers were measured by the gray-scale method.[17] the photosensitivity of PCNPMA of DF 97.5 mol %, exposed for 3 min and then developed for 2 min, had high photosensitivity (11 by the gray scale).

The relationships between the degree of functionalization of coPCNPMA and coPCNNMA and their photosensitivities (3 min exposure) are shown in Figure 4. The photosensitivity of coPCNPMA increased with increasing DF up to 60 mol %. On the other hand, coPCNNMA had its the highest photosensitivity at about DF 55 mol %. In addition, it was found that coPCNNMA had a much higher gray-scale photosensitivity than coPCNPMA, in contrast to the results of the rates of photochemical reaction of these polymers measured by IR spectrometry. In the previous article,[20] where Nishikubo et al. found that self-sensitized photosensitive polymers containing both photosensitive and photosensitizer groups have a higher practical photosensitivity than polymers containing only the pendant photosensitive moiety mixed with low molecular weight photosensitizers, there was a similar contrast with results of photochemical reaction rates measured by IR spectrometry.

Usually, it may be assumed that the rate of photochemical loss of $C{=}C$ in a cinnamate polymer, as measured by IR spectrometry, represents the sum of both intra- and intermolecular photochemical reactions of functionalized polymer chains. On the other hand, the practical photosensitivities of coPCNPMA and coPCNNMA measured by the gray-scale method depend only on the rate of interchain cross-linking.

Therefore it can be concluded that though the apparent rate of photochemically induced consumption of polymer-bond cinnamate is strongly decreased by the introduction of large excess amounts of bulky pendant 4-nitro-1-naphthoxy groups, the intermolecular photochemical reactions of the cinnamic ester moieties in coPCNNMA are much more favored than in coPCNPMA, probably because of a biased conformation of the main chain and pendant cinnamic ester moieties in the former polymer due to greater steric hindrance of its more bulky photosensitizing groups.

As a consequence, we propose here that an appropriate conformation of the polymer chain and the photosensitive group is another important factor to consider in designing highly sensitive polymeric negative-working photoresists, along with high molecular weight,[21] high content of photosensitive moiety,[21] and low T_g.[22]

Registry No. coPGMA, 26141-88-8; TEA, 121-44-8; TMAB, 64-20-0; TEAB, 71-91-0; TPAB, 1941-30-6; TBAB, 1643-19-2; TBAI, 311-28-4; TBAP, 1923-70-2; TBPB, 3115-68-2; benzoic acid, 65-85-0.

References and Notes

(1) Iwakura, Y.; Kurosaki, K.; Imai, Y. *J. Polym. Sci., Part A* **1965**, *3*, 1185.
(2) Kakurai, T.; Yoshida, E.; Noguchi, T. *Kobunshi Kagaku* **1968**, *25*, 412; *Chem. Abstr.* **1968**, *69*, 87681*u*.
(3) Kalal, J.; Svec, F.; Marousek, V. *J. Polym. Sci., Polym. Symp.* **1974**, *No. 47*, 155.
(4) Elvira, J. R.; Baba, S. G.; Disselhoff, R. *Angew. Makromol. Chem.* **1974**, *36*, 199.
(5) Mrkvickova, L.; Kalal, J.; Bednar, B.; Janca, J. *Makromol. Chem.* **1982**, *183*, 203.
(6) Soutif, J. C.; Moussounda, F. M.; Brosse, J. C. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 61.
(7) For example: Iwakura, Y.; Kurita, K. "Reactive Polymers"; Kodanasha: Tokyo, 1977.
(8) Nishikubo, T.; Ibuki, S.; Mizuko, T.; Takaoka, T. *Kobunshi Ronbunshu* **1975**, *32*, 604; *Chem. Abstr.* **1976**, *84*, 19231*g*.
(9) Jones, J. I. *J. Chem. Soc.* **1957**, 2735.
(10) Funahashi, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1488.
(11) Vashchuk, V. Ya.; Moschinsh, N. K. *Vyskomol. Soedin., Ser. B* **1973**, *15*, 275.
(12) Funahashi, K. *Makromol. Chem.* **1979**, *180*, 501.
(13) Nishikubo, T.; Iizawa, T.; Saito, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2291.
(14) Nishikubo, T.; Iizawa, T.; Takahashi, E.; Nono, F. *Polym. J.* **1984**, *16*, 371.
(15) Bender, M. L.; Schonbaum, G. R.; Zerner, B. *J. Am. Chem. Soc.* **1962**, *84*, 2540.
(16) Kakiuchi, H. "Epoxy Resins"; Shokodo: Tokyo, 1975; p 164.
(17) Minsk, L. M.; Smith, J. G.; Van Deusen, W. P.; Wright, J. F. *J. Appl. Polym. Sci.* **1959**, *6*, 302.
(18) Nishikubo, T.; Iizawa, T.; Yamada, M.; Tsuchiya, K. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2025.
(19) Iizawa, T.; Nishikubo, T.; Takahashi, E.; Hasegawa, M. *Makromol. Chem.* **1983**, *184*, 2297.
(20) Nishikubo, T.; Takahashi, E.; Iizawa, T.; Hasegawa, M. *Nippon Kagaku Kaishi* **1984**, 306; *Chem. Abstr.* **1984**, *100*, 175471*q*.
(21) Tsuda, M. *J. Polym. Sci., Part A* **1964**, *2*, 2907.
(22) Nishikubo, T.; Ichijo, T.; Takaoka, T. *Nippon Kagaku Kaishi* **1973**, 35; *Chem. Abstr.* **1973**, 78, 150375*q*.

Secondary Structure of Peptides. 20. Primary–Secondary Structure Relationships of Ala/Gly/Val Copolypeptides[†]

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ABSTRACT: Benzylamine-, triethylamine-, and pyridine-initiated terpolymerizations of alanine *N*-carboxyanhydride (Ala-NCA), glycine *N*-carboxyanhydride (Gly-NCA), and valine *N*-carboxyanhydride (Val-NCA) were conducted in various solvents. The molar compositions of the resulting terpolypeptides were determined from ^{1}H NMR spectra. Their sequences were analyzed by means of ^{15}N NMR spectroscopy, and nearly random sequences were found in all cases. The secondary structure of the solid "as-polymerized" samples was characterized by means of ^{13}C NMR CP/MAS spectroscopy. The α-helix/β-sheet ratio was determined for all three amino acid units separately. In contrast to glycine a substantial fraction (up to 60%) of Val units assumes the α-helical conformation. The composition of the secondary structure partially changes upon reprecipitation. In contrast to the random terpolypeptides the two isomeric sequence polypeptides $(\text{Ala-Gly-Val})_n$ and $(\text{Gly-Ala-Val})_n$ exclusively possess the β-sheet structure. However, in the block copolypeptide $(\text{Ala})_l$-$(\text{Gly})_m$-$(\text{Val})_n$ the $(\text{Ala})_l$ blocks assume the α-helical conformation, whereas the $(\text{Gly})_m$ and $(\text{Val})_n$ blocks exclusively take on the β-sheet structure.

Introduction

Copolypeptides are in principle better models of proteins than homopolypeptides, because their primary structure includes two or more different amino acids. However, their role as protein models suffered in the past from the fact that no routine method of sequence analysis existed, because the procedures used for proteins cannot be applied to copolypeptides prepared by ring-opening polymerization. Furthermore, IR and spectroscopy and X-ray diffraction allowed at best the determination of the most

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