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Polyoxazoline Having a Coumarin Moiety as a Pendant Group. Synthesis and Photogelation[1]

Yoshiki Chujo, Kazuki Sada, and Takeo Saegusa*

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606, Japan

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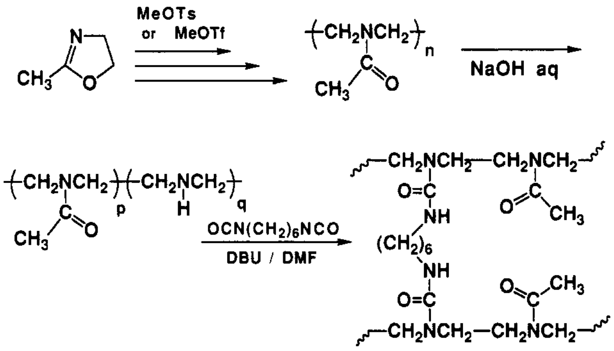
ABSTRACT: Polyoxazoline having a coumarin moiety in the pendant group was synthesized by the reaction of partially hydrolyzed poly(*N*-acetylethylenimine) with (7-coumaryloxy)acetic acid in the presence of dicyclohexylcarbodiimide (DCC) as a condensing agent. The photosensitive polyoxazoline was irradiated with a 450-W high-pressure Hg lamp ($\lambda > 300$ nm) for 7 h to produce polyoxazoline gels. These gels were swollen in water and showed characteristic properties of a hydrogel. Their equilibrium degree of swelling in water was controlled by the irradiation time and also by the degree of substitution of the coumarin moieties. The water uptake was up to 20 times the weight of the dry gel. The photocleavage reaction of the gel, which was monitored by its UV spectrum, was carried out by irradiation with a low-pressure Hg lamp ($\lambda \sim 253$ nm).

Introduction

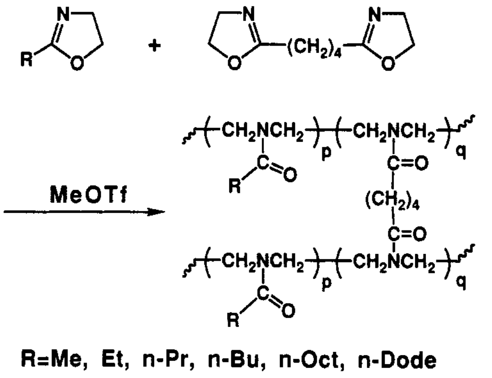
Hydrogels are known to be one of the most interesting polymeric materials and are used in a wide range of applications from household materials to civil engineering applications. Recently, we reported the preparation of a novel non-ionic hydrogel based on poly(*N*-acetylethylenimine) by using two different methods, i.e., the partial hydrolysis/cross-linking method[2] and the copolymerization method,[3] as shown in Schemes I and II, respectively. The product gels showed characteristics of a non-ionic hydrogel, and their degrees of swelling were several orders of magnitude higher than that of dry gels. In the latter method, a copolymerization of 2-alkyl-2-oxazoline (the alkyl substituent varied from methyl to dodecyl) with a bis(oxazoline) produced a wide variety of gels ranging from hydrogel to lipogel. The medium alkyloxazoline produced an "amphigel" (amphiphilic gel), which swelled not only in water but also in some organic solvents.

Here we wish to report a novel method for the preparation of a hydrogel based on polyoxazoline by means of photodimerization of the photosensitive groups in the pendant groups of the polymer chain. Cross-linking by photodimerization has been used commercially in the past decade for a wide variety of purposes in paint, printing, adhesive, and dental industries as well as in the field of photoresist.[4-7] Generally, in negative photoresists, polymers contain a photosensitive group such as cinnamate or chalcone, which causes insolubilization of the polymer by light irradiation. However, very little is known about the preparation of a hydrogel by photo-cross-linking of water-soluble polymer molecules. An example is a water-soluble photo-cross-linkable poly(vinyl alcohol), which was employed as a matrix for immobilizing enzymes.[8,9] The swelling properties of the hydrogels obtained by photo-cross-linking have not been studied so far. In the present study, coumarin was employed as a photosensitive group because it is known to undergo [2 + 2] cycloaddition on UV irradiation.[10,11] In addition, it is also of interest to note that a reversible photodimerization by changing the wavelength of the irradiation light has been known with coumarin.[12] Thus, we studied the reversible interconversion between the hydrogel and the soluble polymer by means of light irradiation.

Scheme I



Scheme II



Experimental Section

General Procedure. UV spectra were measured on a Hitachi 200 UV-vis spectrophotometer. IR spectra were recorded on a Hitachi 260-50 grating spectrophotometer. ^{1}H NMR spectra were obtained on a Hitachi R-600 (60 MHz) or on a JEOL JNM-JX-400 (400 MHz) spectrometer. All ^{1}H NMR spectra were recorded in $CDCl_3$ solutions with tetramethylsilane as the internal standard. GPC analysis was carried out on a Toso CCPD (TSK gel G4000) after calibration with the standard polystyrene samples.

Materials. All solvents and reagents were used as supplied except for the following materials. *N,N*-Dimethylformamide (DMF) was distilled from BaO and then from CaH_2 under reduced pressure. Acetone was distilled from potassium carbonate (anhydrous) under nitrogen. Nitromethane and 1,2-dichloroethane

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were distilled from P_2O_5 under nitrogen. Acetonitrile was distilled from calcium hydride. Thionyl chloride was distilled from triphenyl phosphite. Methyl *p*-toluenesulfonate was distilled under reduced pressure. 2-Methyl-2-oxazoline (5) and diethylamine were distilled from potassium hydroxide. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under nitrogen. Ethyl bromoacetate was distilled under reduced pressure. According to the previous method, poly(*N*-acetylethylenimine) (6) was pepared by the ring-opening polymerization of 2-methyl-2-oxazoline in the presence of methyl *p*-toluenesulfonate as an initiator, which was then subjected to partial hydrolysis with sodium hydroxide solution.[2]

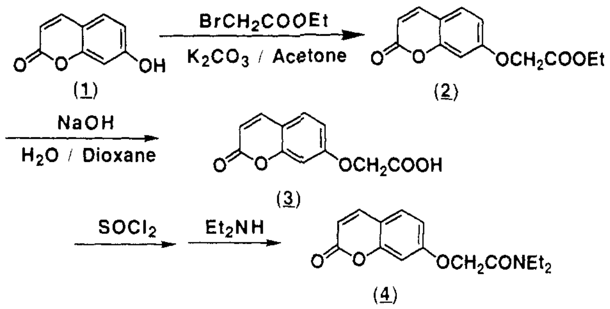
Ethyl (7-Coumaryloxy)acetate (2). To a solution of 9.826 g (60.6 mmol) of 7-hydroxycoumarin (1) and 7.2 mL (64.6 mmol) of ethyl bromoacetate in 270 mL of freshly distilled acetone was added 8.75 g of potassium carbonate (anhydrous), and the reaction mixture was refluxed for 2 h. After removal of the salts by filtration, the solution was concentrated under reduced pressure and dried in vacuo. The pale yellow solid was recrystallized from ethanol. Ethyl (7-coumaryloxy)acetate (2) was obtained as a white solid (10.627 g, 70.6%), mp 113–115 °C. ^1H NMR: δ 1.30 (t, 3 H, J = 7.5 Hz), 4.28 (q, 2 H, J = 7.5 Hz), 4.67 (s, 2 H), 6.26 (d, 1 H, J = 10 Hz), 6.77 (s, 1 H), 6.89 (d, 1 H, J = 9 Hz), 7.40 (d, 1 H, J = 9 Hz), 7.60 (d, 1 H, J = 10 Hz). IR (KBr): 3080, 2980, 2950, 1730, 1706, 1610, 1400, 1220, 1190, 1120, 1070, 980, 840 cm^{-1}.

(7-Coumaryloxy)acetic Acid (3). A mixture of 2.16 g (8.7 mmol) of ethyl (7-coumaryloxy)acetate (2) and 5 g (125 mmol) of sodium hydroxide was dissolved in ca. 200 mL of water/dioxane (1/1). After the solution was stirred overnight, the solvent was removed under reduced pressure. The yellow residue was dissolved in 20 mL of distilled water and acidified with concentrated hydrochloric acid under ice cooling. The white precipitate was collected by filtration, washed well with cooled water, and dried in vacuo to produce 1.846 g (96%) of (7-coumaryloxy)acetic acid (3), mp 209–213 °C. The analytical sample was recrystallized further from ethanol–benzene. ^1H NMR ($CDCl_3$-DMSO-d_6): δ 4.73 (s, 2 H), 6.20 (d, 1 H, J = 10 Hz), 6.80 (s, 1 H), 6.92 (d, 1 H, J = 9 Hz), 7.48 (d, 1 H, J = 9 Hz), 7.80 (d, 1 H, J = 10 Hz), 12.79 (br s, 1 H). IR (KBr): 3080, 2980, 1720, 1610, 1400, 1240, 1220, 1120, 1070, 990, 830 cm^{-1}.

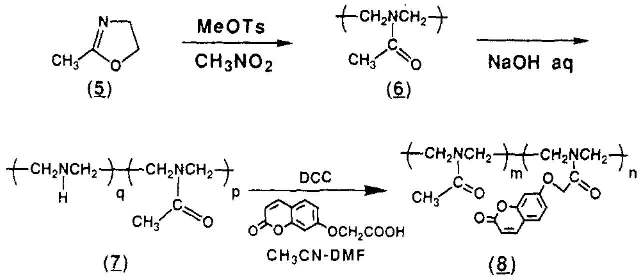
***N,N*-Diethyl(7-coumaryloxy)acetamide (4).** A solution of 0.453 g (11 mmol) of (7-coumaryloxy)acetyl chloride (IR (KBr) 1805, 1720 cm^{-1}), which was prepared by the treatment of the above acid (3) with thionyl chloride, in 30 mL of dry THF was added dropwise to a precooled solution (0 °C) of 75 mg (11 mmol) of diethylamine in THF (40 mL) for 30 min. After being stirred for 6 h, the solution was filtered through a filter paper to remove the diethylamine hydrochloride salt. The solvent was removed by evaporation under reduced pressure. The resulting yellow oil was extracted with ethyl acetate (ca. 40 mL) and washed with aqueous sodium bicarbonate solution and then with brine (10-mL each). After being dried over sodium sulfate, the solution was concentrated and dried in vacuo to produce 0.343 g (70.6%) of *N,N*-diethyl derivative (4) as a white hygroscopic solid, mp 56.8–58.0 °C. ^1H NMR: δ 1.14 (t, 3 H, J = 7.5 Hz), 1.25 (t, 3 H, J = 7 Hz), 4.28 (q, 4 H, J = 7 Hz), 4.73 (s, 2 H), 6.24 (d, 1 H, J = 10 Hz), 6.82 (s, 1 H), 6.85 (d, 1 H, J = 9 Hz), 7.43 (d, 1 H, J = 9 Hz), 7.64 (d, 1 H, J = 10 Hz). IR (KBr): 3080, 2980, 2930, 1712, 1607, 1400, 1280, 1230, 1200, 1135, 1040, 980, 860 cm^{-1}. UV (methanol): λ_{max} = 319 nm (ϵ = 15 000), 293 nm (sh) (ϵ = 10 000).

Poly(*N*-acetylethylenimine)–Poly(*N*-((7-coumaryloxy)acetyl)ethylenimine) Copolymer (8). A typical procedure is as follows. A benzene (5 mL) suspension of a mixture of 0.535 g of 10.2 mol % hydrolyzed polyoxazoline (7) (0.663 mmol of NH equivalent) and 0.276 g (1.25 mmol) of (7-coumaryloxy)acetic acid (3) was freeze-dried. After dry nitrogen was introduced, the mixture was dissolved in a mixture of dry 1,2-dichloroethane (20 mL) and freshly distilled DMF (6 mL) under nitrogen atmosphere and cooled at 0 °C. To this solution was added 0.389 g (1.88 mmol) of dicyclohexylcabodiimide (DCC). After the mixture was stirred overnight, the resulting dicyclohexylurea was removed by filtration, and the filtrate was concentrated to yield a pale orange polymer, which was redissolved in methanol and reprecipitated into diethyl ether (two times). Coumarin-modified poly(*N*-acetylethylenimine) (8) was obtained after freeze-drying with benzene. The yield was 543 mg (81%). ^1H NMR and UV spectra are shown in the text.

Scheme III



Scheme IV



Gelation by Photodimerization. A typical procedure is as follows. Coumarin-modified polyoxazoline (8) (48.46 mg, 8.8 mol % coumarin content) was dissolved in ca. 0.6 mL of methanol, from which a film was cast over a glass slide (76 × 26 mm) at room temperature under air. The resulting polyoxazoline film was irradiated with 450-W high-pressure mercury lamp (Ushio UM-452) through a Pyrex cooler to cutoff the wavelengths below 300 nm for 3–7 h. After irradiation, the film was immersed in methanol to remove the unreacted soluble part of the polymer. After being washed repeatedly with fresh methanol, the gel was dried in vacuo. The yield of polyoxazoline gel was 43.56 mg (81%).

Swelling Properties. The equilibrium swelling properties in water were measured as follows. The carefully dried and weighed gel (42.7 mg) was immersed in ca. 100 mL of deionized water (the resistance was more than 12 MΩ) for 24 h at room temperature. The weight of the swollen gel was measured (122.7 mg) after filtration by 1G4 glass filter under reduced pressure (ca. 17 mmHg, 2 min). The degree of swelling, which was calculated by the following equation [Wg(swollen) − Wg(dry)]/Wg(dry), was measured to be 1.9.

Photocleavage Reaction. The gel film prepared by the photocoupling reaction (ca. 2-h irradiation on the quartz plate, under the same conditions described above) was irradiated at $\lambda \sim$ 253 nm with a low-pressure mercury lamp (Fuji UVL-10H). The change in the absorption in its UV spectrum was measured from 240 to 370 nm.

Results and Discussion

Synthesis of Coumarin-Modified Polyoxazoline. Preparation of various coumarin derivatives is represented in Scheme III. Commercially available umbelliferonen (7-hydroxycoumarin) (1) was employed as a starting material. The coumarin moiety was introduced to polyoxazoline by the reaction of partially hydrolyzed polyoxazoline with (7-coumaryloxy)acetic acid (3) as shown in Scheme IV. *N,N*-Diethyl(7-coumaryloxy)acetamide (4) was prepared as a model compound for the coumarin-modified polyoxazoline. A series of the partially hydrolyzed polyoxazolines with various degrees of hydrolysis were prepared by the ring-opening polymerization of 2-me-

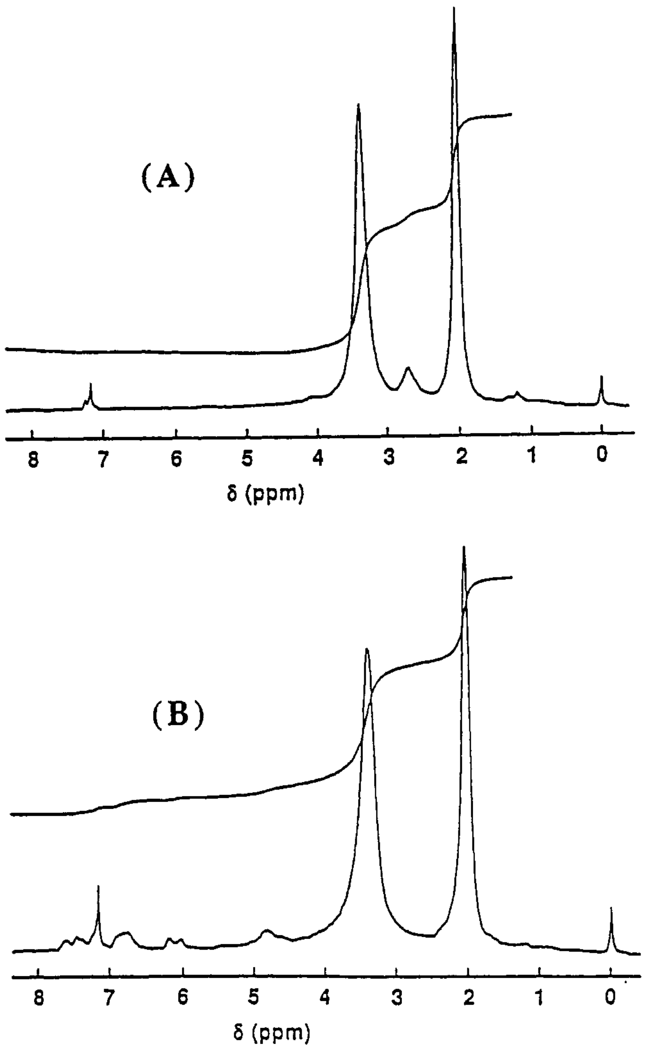


Figure 1. ^{1}H NMR spectra of (A) partially hydrolyzed (10.2 mol %) polyoxazoline (5) and (B) coumarin-modified (8.8 mol %) polyoxazoline (8).

thyl-2-oxazoline followed by alkaline hydrolysis of polyoxazoline, according to the procedure reported before.[2] Thus, the photosensitive polyoxazolines were obtained in moderate yields.

Figure 1 illustrates ^{1}H NMR spectra of the coumarin-modified polyoxazoline (degree of substitution, 8.8 mol % by UV) (8) and of the starting partially hydrolyzed polyoxazoline (degree of hydrolysis, 10.2 mol %) (5). The peak of the methylene protons adjacent to the secondary amino group (δ 2.8) disappeared completely in 8. At the same time, the ring protons (δ 6.2–7.6) and the oxymethylene protons (δ 4.7) of the coumarin moiety were observed. The substitution degree of photosensitive groups could be calculated by the integral ratio between these coumarin protons and the remaining *N*-acetyl protons.

The UV spectrum of the obtained photosensitive polymer (1.2 mol %) in methanol is represented in Figure 2, in which the absorption maximum of the 7-oxycoumarin moiety is observed at 319 nm. A model compound, *N*,*N*-diethyl(7-coumaryloxy)acetamide (4), had its absorption at the same wavelength, 319 nm (ϵ = 15 000). The degree of substitution could be estimated from the UV spectrum of the photosensitive polymer by using the absorption coefficient of a model compound (4). Table I summarizes the results of the preparation of the coumarin-containing polyoxazoline together with their degrees of substitution.

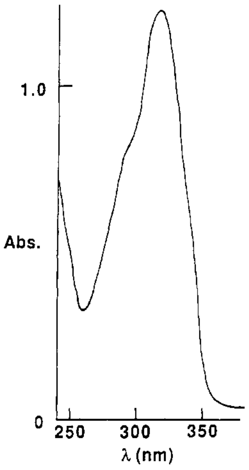


Figure 2. UV absorption spectrum of coumarin-modified (1.2 mol %) polyoxazoline (M_n = 25 300) in methanol at room temperature (1.27 mg/2 mL).

Table I
Preparation of Coumarin-PAEI

				n/(m + n)	
run	PAEI-PEI $\bar{M}_n$[a]	copolymer $q/(p + q)$[b]	yield, %	UV[c]	^{1}H NMR[d]
1	25 300	0.021	81	0.012	
2	25 300	0.048	78	0.040	
3	25 300	0.102	81	0.086	0.088
4	25 300	0.143	87	0.142	0.134
5	25 300	0.324	71	0.304	
6	15 800	0.051	92	0.039	

[a] Determined by GPC (PSt standard). [b] Determined by titration. [c] Determined by UV at λ_{max} = 319 nm (ϵ = 1.5 × 10^4). [d] Determined by ^{1}H NMR (*acetyl proton versus ring proton*).

The degrees of substitution estimated from UV spectra were found to be close to the values calculated from ^{1}H NMR. These values also corresponded well to the degrees of hydrolysis of the starting partially hydrolyzed polyoxazoline. In the titration of the secondary amino groups in the resulting polymer, no amino group could be detected within experimental error. These results are taken to confirm a completion of the condensation reaction for the preparation of 8. The results of the swelling properties of the obtained gels can be explained by the values of the degree of substitution (vide infra). In other words, the degree of functionality of the photosensitive polymers could be controlled by the degree of hydrolysis in 5.

From GPC analysis, a significant change in the molecular weights of 8 was observed in comparison with that of the parent polymer (5). The molecular weight distribution (M_n = 22 500, M_w = 34 500, M_w/M_n = 1.5) of 8 was also similar to that of the starting polymer. The GPC trace by the UV detector at 319 nm indicates the introduction of the photosensitive group to the polyoxazoline. Thus, it is clear that no significant chain degradation or cross-linking reaction occurred during the condensation step in the preparation of these functionalized polyoxazolines. It should also be noted that no photoactive impurity proved to contaminate in 8 from its GPC trace.

Photogelation of Coumarin-Modified Polyoxazoline. The photocoupling reaction was carried out in a bulk film (cast from methanol solution on a glass slide) at room temperature by irradiation of 450-W high-pressure mercury lamp at λ > 300 nm. The reaction could be monitored by studying the UV absorption change of the cast film of polyoxazoline on a quartz plate. As shown

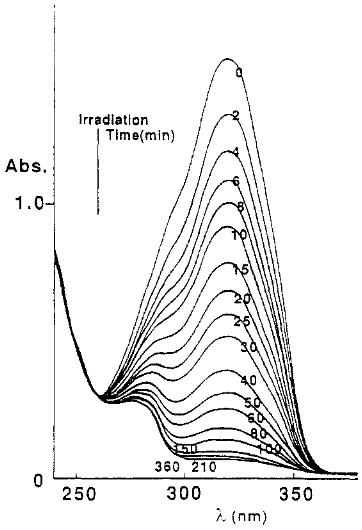


Figure 3. UV absorption spectral change of coumarin-modified (3.9 mol %) polyoxazoline (M_n = 15 800) by irradiation with a 450-W high-pressure Hg lamp.

Table II
Photogelation Reaction[a]

reaction time, min	conversn,[b] %	gel yield, %	swelling degree[c] in H_2O
15	52	0[d]	
30	59	41	14.1
70	85	67	8.0
350	>95	69	4.0

[a] In bulk film, 450-W high-pressure Hg lamp. Prepolymer: $\bar{M}_n$ = 1.58 × 10⁴, $n/(m + n)$ = 0.039.[b] [b] Calculated from UV absorption at λ_{max} = 319 nm (ϵ = 1.5 × 10⁴). [c] g of H_2O/g of dry gel. [d] Soluble in MeOH.

Table III
Photogelation Reaction[a]

run	$\bar{M}_n$[b]	$n/(m + n)$[c]	yield, %	swelling degree[d]
1	25 300	0.012	67	20.7
2	25 300	0.040	91	3.9
3	25 300	0.086	90	2.9
4	25 300	0.142	88	1.9
5[e]	24 000	0	0	
6	15 800	0.039	69	4.0

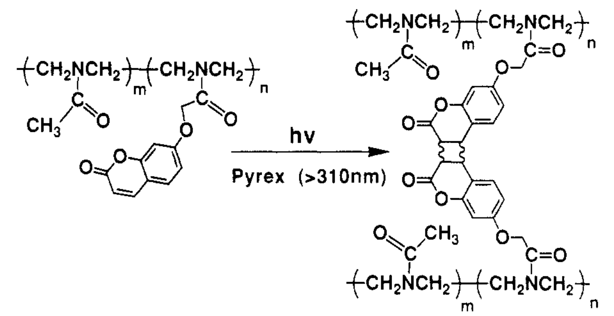
[a] In bulk film, irradiated for 5 h (450-W high-pressure Hg lamp). [b] Determined by GPC (PSt standard). [c] Determined by UV and ^1H NMR. [d] g of H_2O/g of dry gel. [e] Prepolymer (20% hydrolyzed or not hydrolyzed) without the coumarin moiety formed no gel.

in Figure 3, the absorption at 319 nm decreased with an increase in the time of irradiation, which showed the disappearance of the double bond of coumarin. Coumarin is known to form four isomeric dimers by light irradiation.[10,11] However, these four isomers in the gel state were not identified in this study.

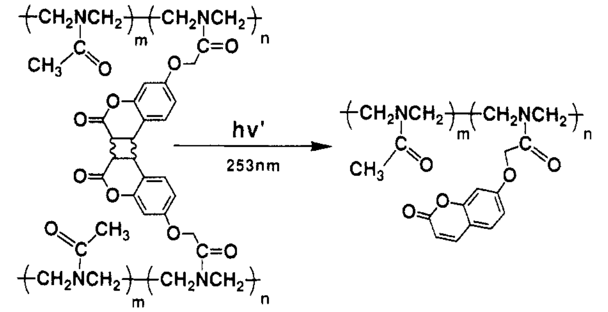
Table II shows the results of gelation and the swelling properties of the obtained films together with the conversion of coumarin groups calculated from UV spectra. In the case that the irradiation time was shorter than 15 min, the conversion of coumarin was less than 50%, and consequently no insoluble gel was produced. After longer irradiation, the insoluble gels, which swelled much in water, had enough strength to be handled. With an increase in the reaction time, the yield of the polyoxazoline gel was increased and its swelling property in water was decreased. Thus, the average distance between the nearest two branches is to be controlled by the time of irradiation.

Table III shows the results of photoreaction of coumarin-modified polyoxazolines with a variety of degrees of substitution and the swelling properties of the obtained gels.

Scheme V



Scheme VI



In all cases except for run 5, the polyoxazoline gel was obtained in a good yield. No gelation was observed in the absence of the photosensitive group in the polymer pendant, i.e., in the cases of hydrolyzed polyoxazoline and of non-hydrolyzed parent polymer. A mixture of partially hydrolyzed prepolymer and coumarin derivatives also formed no gel product. These results indicate that the intermolecular cross-linking by photodimerization of the coumarin moieties in 8 caused the formation of a stable hydrogel (Scheme V).

Swelling Property in Water. As shown in Table III, the degree of swelling in water was increased with a decrease in the content of the photosensitive group in the polymer. For example, the water uptake by the gel prepared from polyoxazoline with 1.2 mol % coumarin content was 20 times as high as its own weight. The swelling property could be controlled by the degree of functionalization of polyoxazoline.

The degree of swelling of the coumarin-modified polymer (M_n = 25 300, 4.0 mol % coumarin) was almost equal to that of the polymer which had the smaller molecular weight with a similar content of the coumarin group (M_n = 15 800, 3.9 mol %) (runs 2, 6). This result means that the average distance between the nearest two cross-linking points, i.e., the swelling property, was controlled primarily by the content of the coumarin moiety.

Photocleavage Reaction. As mentioned in the introductory section, coumarin is known to cause a photoreversible reaction. The cyclobutane ring in the photodimer of coumarin is cleaved by irradiation of light with a wavelength shorter than 300 nm to regenerate coumarin almost quantitatively. The polyoxazoline gel was subjected to the photocleavage reaction by the irradiation of a low-pressure mercury lamp at λ ~ 253 nm. Figure 4 shows the change in UV absorption of the gel film upon irradiation. The absorption at 319 nm due to the coumarin moiety was regenerated by irradiation; thus, it has been established that the photocleavage reaction of cyclobutane ring in the gel does occur and the starting coumarin moiety is regenerated. However, the absorption intensity did not completely return to the original level after

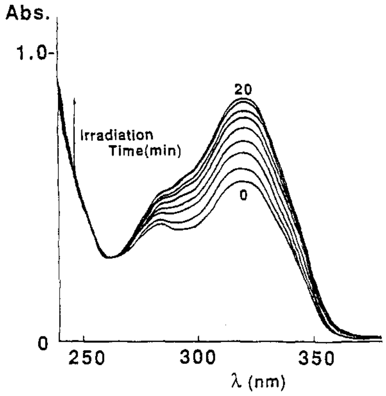


Figure 4. UV absorption spectral change of coumarin-modified polyoxazoline by irradiation with a low-pressure Hg lamp.

irradiation for a long time (55–60% of the dimer was converted to the starting material, calculated from the UV spectrum). The photo-cross-linked gel prepared by a shorter irradiation time, which was insoluble in methanol, was changed to the soluble polymer after the photocleavage reaction. From this result, when the content of the photodimer in the gel was not so high, the cross-linking point was destroyed by the reverse reaction on irradiation of light at 253 nm and the hydrogel turned out to be soluble (Scheme VI).

Conclusions

The photocoupling reaction of the coumarin-modified polyoxazoline in the present study could offer a method for the preparation of a non-ionic hydrogel under mild conditions (at ordinary temperature). The swelling properties of the obtained gels were easily controlled by the irradiation time or by the content of coumarin moieties. Taking into account the compatibility of polyoxazoline with other organic commodity polymers,[13,14] these hydrogels prepared by photogelation are quite interesting polymeric materials. In addition, it should be noted that the reverse reaction of photodimerization proceeded upon irradiation with a low-pressure Hg lamp to regenerate a linear, soluble polyoxazoline. These results make it possible to control the state of the gel or that of the soluble polymer by means of irradiation. The photogelation reactions of polyoxazolines bearing other photosensitive groups such as anthracene, maleimide, or cinnamic acid are now under investigation in our group.

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