Preparation and Reactions of Polymers Having 1-Aroyl-2-(3-pyridyl)ethylenes as Photosensitive Groups

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Synopsis

The reactions of 1-aroyl-2-(3-pyridyl)ethylenes (APE) with polychloromethylstyrene (PCMS) yield polymeric systems which undergo rapid crosslinking upon short exposure to ultraviolet (UV) light. The photochemical reaction of polymers as well as model compounds was followed by the measurement of UV absorption of APE and the analysis of extinction coefficient difference (ED) diagrams.[1]

INTRODUCTION

Many types of water-base-soluble photocross-linkable polymers have been prepared using quaternary nitrogen, hydroxy, sulfonic acid, and carboxylic acid as the solubilizing function.[2] Photosensitive polymers having quaternary salts of various types of compounds in the side chains have been prepared.

There are two main methods for the preparation of photosensitive quaternized polymers: direct quaternization with photosensitive chromophores and the reaction of quaternized polymers with aldehydes.

Among those preparative methods, some difficulties encountered in preparing the *N*-vinylpyridiniumarylsulfonate-type polymers involved: the tendency to gel if quaternizatioon is attempted at elevated temperature: the necessity of using an excess of quaternizing nucleophiles in order to get appreciable quaternization.[3] Further, quaternization of poly(2-chloroethyl vinyl ether) with γ-stilbazole requires high reaction temperatures and prolonged heating results in a deep coloration.[4] The present paper describes that 1-aroyl-2-(3-pyridyl)ethylene (APE) is highly reactive to polychloromethylstyrene (PCMS) and the polymers obtained react upon irradiation of UV light.

EXPERIMENTAL

Materials

Commercially available monomer of chloromethylstyrene (*meta/para:* 7/3) was distilled under reduced pressure (5–6 mm) and the fraction boiling between 76 and 78°C was used. PCMS of $[\eta]$ = 0.13 was prepared by radical polymerization in benzene at 60°C for 16 hr in the presence of AIBN (0.5

wt/wt%) and purified by repeated precipitation in *n*-hexane. Anal. Calcd. for $C_9H_9Cl_1$: C,70.83; H,5.90. Found; C,70.66; H,6.07%.

The derivatives of 1-aroyl-2-(3-pyridyl)ethylene were prepared by a procedure similar to that described in the literature.[5]

The typical procedure is as follows. To a mixed solvent of 25 mL of ethanol and 50 mL of aqueous hydroxide (10%) was added 11 g of benzophenone and 10 g of pyridine-3-aldehyde, and the mixture was then stirred keeping the temperature below 5°C.

Within 15 min the oily substances crystallized. The stirring was further continued at 5°C for 1 hr. The pale yellow precipitates were collected, washed with water, and dried *in vacuo*.

QUATERNIZATION

In a typical experimental procedure, the mixture of 0.334 g of 1-benzoyl-2-(3-pyridyl)ethylene and 0.2 g of PCMS in 10 mL of dimethylformamide (DMF) was heated at 60°C with stirring. After the reaction had continued for 18 hr, the solution was poured into 50 mL of ether. The precipitate was collected, rinsed, and dried in vacuo. Other polymers were similarly prepared. To improve the solubility of quaternized polymers, further quaternization of remaining haloalkyl groups with pyridine was carried out. The results were presented in Table IV.

SPECTROSCOPY

The ultraviolet (UV) absorption spectra were recorded by a Shimazu UV-220 spectrophotometer. The infrared (IR) spectra were obtained from a Hitachi 260-30 infrared spectrophotometer.

PHOTOREACTION

A 3 mL measure of sample solution in a 1 × 1 cm quartz cell was irradiated with the light from a Jasco spectroirradiator (CRM-FA) which was composed of a 2 kW xenon lamp and a grating monochrometer.

SENSITIVITY MEASUREMENT

Various methods for the evaluation of photosensitivity are available.[2] A solution of polymer in dimethylacetamide (DMA) was cast on a quartz glass plate or an aluminum plate with a spin coater and then annealed for 20 min at 70°C.

The thin film was then irradiated through a photographic step tablet No. 1A (Kodak) with a fixed energy of light from a Ushio UIV-270 parallel beam irradiator with a 500 W xenon lamp and dipped in methanol or water for a fixed time to remove unreacted components. The relative sensitivity values listed in Table V are based on a comparison with that of P-I.

RESULTS AND DISCUSSION

Synthesis of APE

As listed in Table I, the derivatives of APE were generally prepared in good yields. Higher temperatures than 10°C reduce the yields. The physical properties and the analytical data are given in Table II. In IR spectra the absorptions at around 1620 cm^{-1} due to the formation of carbon-carbon double bonds appeared and the other bands caused by the C=O also appeared in the 1660–1670 cm^{-1} range. In UV spectra, the peak absorptivity of compounds III and IV are larger than those of I and II. The agreement between the calculated and found in elemental analysis was within the usual limit of variation.

QUATERNIZATION OF POLYMERS

The results of reactions of PCMS with 1-benzoyl-2-(3-pyridyl)ethylene were given in Table III. As can be seen, even at a reaction temperature of 60°C polymers were quantitatively quaternized. Elevated temperatures such as 90° and 100°C reduce the reaction time. Prolonged heating is required to obtain highly quaternized polymers more than 80 mol per cent. Such high reactivity of APE toward PCMS is ascribed to the increased nucleophilicity of APE. As listed in Table III, the polymers with lower degree of quaternization were insoluble in methanol but sufficient quaternization gave methanol-soluble polymers. Under the experimental conditions conducted, there is no tendency to gel.

PHOTOREACTION

Photoreaction of 3-(2-benzoylvinyl)-N-benzylpyridinum chloride as a model compound in methanol was illustrated in Figure 1. An absorption maximum occurs at 279 nm. From Figure I and Table III it is obvious that λ_{max} of 1-benzoyl-2-(3-pyridyl)ethylene shifts from 298 to 279 nm by making the 3-(2-benzoylvinyl)-N-benzylpyridinum cation. Removing the electrons from the nitrogen of APE is responsible for the blue shift.[6]

The ED diagrams derived from spectral change are also illustrated in

TABLE I
Synthesis of 1-Aroyl-2-(3-pyridyl)ethylenes

RCOCH$_2$ + OHC—⟨◯⟩—N ⟶ RCOCH=CH—⟨◯⟩—N

R; I:Phenyl, II:P-Cl-Phenyl, III:P-CH$_3$O-Phenyl, IV: ⟨◯◯⟩
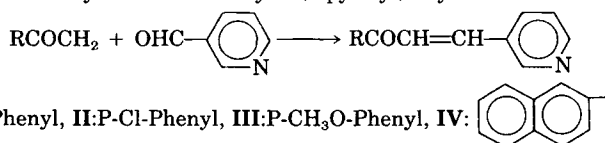
	Reaction temperature (°C)	Reaction time (min)	Yield (%)	Solvent for recrystallization
I	0–5	60	80	EtOH
II	0–5	30	82	Benzene
III	5	120	84	EtOH
IV	5	40	81	EtOH

TABLE II

Physical Properties and Analytical Data of 1-Aroyl-2-(3-pyridyl)ethylenes

R	Mp(°C)	γ(C=C) γ(C=O)	λ_{max} nm (ε)MeOH	Analysis (%)					
				Calcd.			Found.		
				C	H	N	C	H	N
I	102.5–103.5	1610 1670	298 (21000)	80.36	5.30	6.69	80.09	5.17	6.73
II	122–124	1610 1670	302 (19000)	69.00	4.14	5.75	69.28	3.80	5.89
III	111–112	1620 1665	313 (68000)	75.30	5.47	5.85	75.21	5.49	5.79
IV	113.5–115.5	1620 1660	308 (83000)	83.38	5.05	5.40	83.28	4.94	5.25

TABLE III

Quaternization of Poly(chloromethylstyrene) with 1-Benzoyl-2-(3-pyridyl)ethylenes
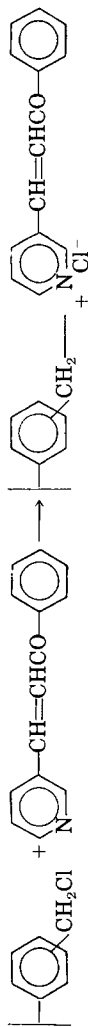
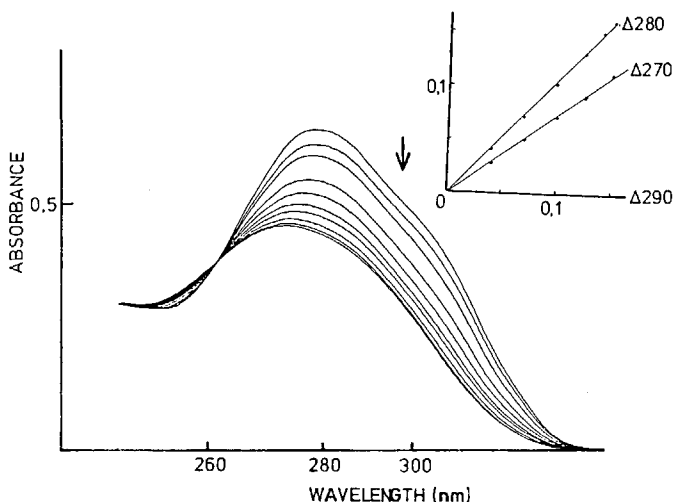| Weight (g) PCMS	Substrate (g)	Reaction temp. (°C)	Reaction time (hr)	Solvent	Incorporated substrate (mol%)	Conversion (%)	Solubility
0.25	0.067	60	18	DMF	20	100	DMF
0.25	0.067	100	6	DMF	20	100	DMF
0.25	0.2	60	18	DMF	60	100	DMF, MeOH
0.25	0.2	90	6	DMF	60	100	DMF, MeOH
0.25	0.268	60	47	DMF	78	98	DMF, MeOH
0.25	0.334	60	47	DMF	97	97	DMF, MeOH

Fig. 1.   UV spectral change and ED diagram of 3-(2-benzoylvinyl)-*N*-benzylpyridinum chloride upon irradiation with light (>300 nm) in methanol (2.1 × 10⁻⁴ M): irradiation time, 0, 10, 30 s, 1, 1.5, 2, 3, 4, 5, 10 min.

Figure 1. The plots of Δ280 and Δ270 versus Δ290 are linear and the other plots for the wavelength longer than 300 nm are also linear; this fact indicates that the system of photoreaction of 3-(2-benzoylvinyl)-*N*-benzyl-pyridinum chloride consists of a sole reaction. From the photostationary state and the linear ED diagrams, it is obvious that direct photoreaction of 3-(2-benzoylvinyl)-*N*-benzylpyridinum chloride in methanol results in *cis-trans* isomerization. Figure 2 illustrates the spectral change due to the photoreaction of poly[3-(2-benzoylvinyl)-*N*-vinyl-benzylpyridinum chloride] (P-I) by the irradiation of UV light of wavelength longer than 300 nm. The absorption maximum of P-I in water is at 260 nm, which is shorter in wavelength compared to that in ethyl cellosolve (Fig. 3).
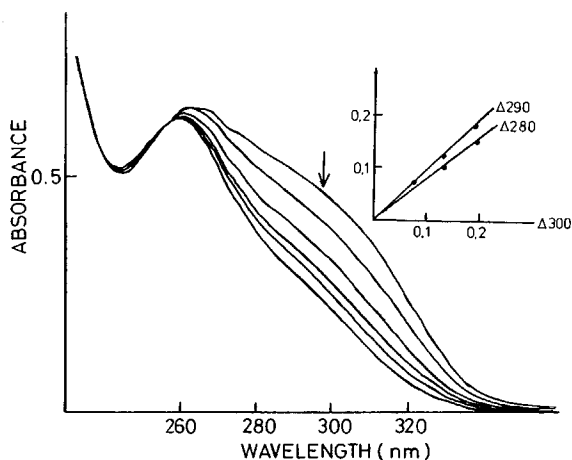

Fig. 2.   UV spectral change by the photoreaction (>30 nm) of P-I ([I] = 50 mol%) in water and ED diagram: irradiation time, 0, 20, 50 s, 1.5, 2.5, 4.5 min.
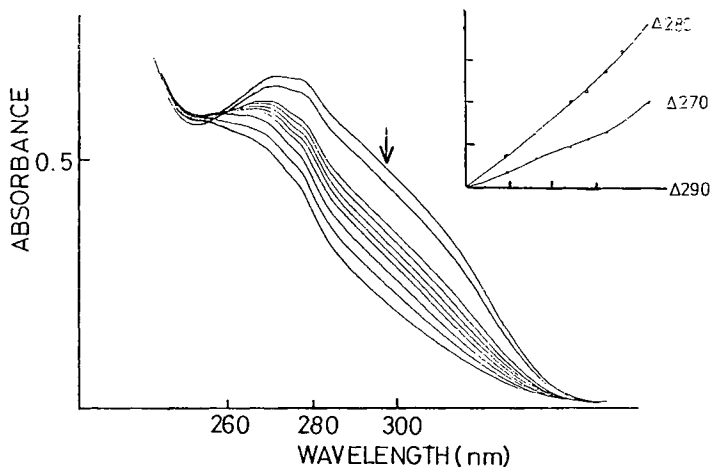
Fig. 3.   UV spectral change and ED diagram by exposure of the ethyl cellosolve solution of P-I to light (>300 nm): ([I] = 56 mol%): irradiation time, 0, 0.5, 1, 2, 3, 4, 5, 6, 7, 15 min.

This blue shift may be correlated to the n-π* states of the chromophores of polymers.[7]

As shown in Figure 2, the ED diagrams for the plots of Δ290 and Δ280 versus Δ300 indicate the linear relationships.

Prolonged irradiation longer than 270 s does not change the UV spectra; these results suggest the photoreaction of P-I in water reached the photostationary state.

Even in this photostationary state, the UV spectra in the region 260 nm still shows considerable absorption. This absorption band can be regarded as unchanged benzenoid absorption because benzyl groups or monosubstituted benzenes display intensive absorption in this region.[8]

Irradiation with light of 240 nm to P-I in water, which was irradiated with light of longer wavelength than 300 nm for 270 s, does not cause the spectral change: this indicates the photoreaction systems do not contain the cyclobutane formation.[9]

As illustrated in Figure 3, the absorption maximum of P-I in ethyl cellosolve appeared at 272 nm. The absorption band at the longest wavelength decreased gradually with the slight increase of a new band at 252 nm. The ED diagram derived from the spectral change (Fig. 3) illustrates that the plots of Δ280 versus Δ290 follow a slight curve and that of Δ270 is also not linear. These results can be interpreted as the competition of cyclodimerization with *trans-cis* isomerization.[9] Since the conformation of polyelectrolytes is sensitive to the nature of solvents, the photoreactivity of the quaternized polymer will be governed by the media. From the comparison of photoreactivity of quaternized polymers in various solvents (Figs. 1–3), it is clear that chromophore association in ethyl cellosolve is much more enhanced than that in water. Figure 4 shows the spectral traces for the photoreaction of P-I with the light of 300 nm in a film state. The absorption maximum of P-I in a film state appeared at 278 nm, which is longer than that in ethyl cellosolve. The absorption band at the longest wavelength decreased with increase of the band in the region 251 nm.
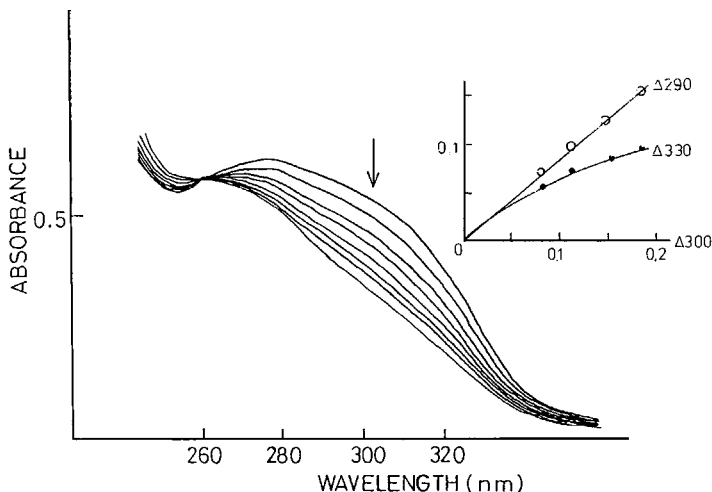
Fig. 4. UV spectral change caused by the photoreaction of P-I in a film state (>300 nm) and ED diagram: ([I] = 60 mol%): irradiation time, 0, 10, 25, 50 s, 1.3, 2.3, 2.6, 7 min.

The new band is ascribable to the cyclodimerization.[9]

During the course of photoreaction, an isosbestic point was, seemingly, observed. But the plot of $\Delta330$ versus $\Delta300$ in the ED diagram indicates that the photoreaction systems comprised at least two reaction processes such as *trans-cis* isomerization and cyclobutane formation leading to insolubilization. As expected, the thin film thus irradiated was not soluble in any solvent. The family of polymers having 100 mol% APE(A) was treated with methanol after photoreaction to remove unreacted components and the other (B) was with water (Table V). For both A and B, the sensitivity of P-III and P-IV are higher than those of P-I and P-II. This behavior may be ascribable to some extent to the absorptivity of chromophores. As already

TABLE IV
Solubility of Photocrosslinkable Polymers
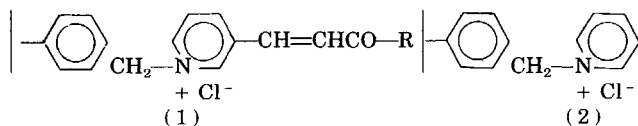
A: (1)—100 mol%, (2)—0 mol%
B: (1)—50 mol%, (2)—50 mol%

R^a	A	B
P-I	MeOH	H_2O
P-II	MeOH	H_2O
P-III	MeOH	H_2O
P-IV	MeOH	H_2O

[a] Roman numerals are identical with those of Table I.

TABLE V
Relative Sensitivity of Photocrosslinkable Polymers

R	A	B
P-I	1	1
P-II	2	2
P-III	9	9
P-IV	9	9

See Table IV for legend.

listed in Table II, the absorptivity of **III** and **IV** are higher than those of **I** and **II**.

However, the sensitivities are not controlled only by the absorptivity of chromophores. The photosensitivities of cross-linkable polymers, in general, are influenced by a great number of factors such as T_g, molecular weight, polymer solubility, the photosensitivity of chromophores, and the like. The sensitivities of quaternized polymers with APE are in the order P-IV=P-III > P-II > P-I under the experimental conditions.

In conclusion, quaternization of PCMS with APE occurred quantitatively and caused the blue shifts of chromophores.

The photoreaction of the polymers quaternized with APE in solvents is controlled by the nature of solvents. The photo-crosslinkability of polymers having APE in a film state correspond to the absorptivity of chromophores.

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