PHOTOREACTION AND CHARACTERIZATION OF POLY(VINYL ALCOHOL) BEARING *p*-PHENYLENEDIACRYLATE ESTER

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1. Introduction

Many conjugate olefins are known as photoreactive crystals which undergo cycloaddition between double bonds giving various types of products, such as linear crystalline polymers, oligomers, dimers [1–3]. Nakanishi *et al.* have investigated extensively the photoreaction of diolefins in the crystalline state [4] and in the Langmuir–Blodgett (LB) films [5–11]. Di- and monoalkyl esters of 3,3'-(*p*-phenylene)diacrylic acid (*p*-PDA) have many interesting characteristics in thermal and photochemical properties. If the *p*-PDA chromophore can be introduced into a polymer system, it will be easily formed into a film state and we can expect different photochemical behavior of these compounds. For this purpose we have synthesized poly(vinyl alcohol) (PVA) having pendent monoalkyl ester of *p*-PDA (*p*-PDAmC_n; n = 6, 10), and have studied photoreaction and characterization of the polymer. In this communication, we describe the photoreaction of *p*-PDAmC_n-PVA in a solution and as a spin-coated film.

p-PDAmC_n-PVA

2. Method

Materials — Di- and monoalkyl ester of *p*-PDA were prepared as described previously [8]. *p*-PDAmC_n-PVA was synthesized from fully saponified PVA of *P* = 1700 and *p*-PDAmC_n by the method of Watanabe *et al.* [12]. The polymer was purified by washing with 2-propanol using a Soxhlet extractor and reprecipitation from chloroform into methanol, and dried *in vacuo*. The degree of esterification was determined spectrophotometrically by use of the absorption coefficient of a dialkyl ester of *p*-PDA (*p*-PDAdiC_n) at 320 nm in dichloromethane.

Film Preparation — The polymer film was prepared from a chloroform solution on a quartz plate by means of spin coating at 1000 rpm for 30 s. The thickness was measured with an Alpha-Step 300 Step-Height Profiler made by Tencor Instruments.

Irradiation — Photoirradiation was performed with 313 nm light from a 500-W super-high-pressure mercury lamp (Ushio USH-500D) filtered through a Hoya U-340 glass filter and a 1-cm

pathlength filter solution containing of 0.265 g/l $K_2Cr_2O_7$ and 0.5 wt% K_2CO_3 . The light intensity was determined by the method of Heller and Langan [13].

Spectroscopy — Absorption spectra were recorded on a Shimadzu UV-160A spectrophotometer. Fluorescence spectra were obtained with a JASCO FP-777 spectrofluorometer. 1H -NMR spectra were measured with a JEOL JNM-GSX270 spectrometer (270 MHz). IR spectra were recorded on a Perkin-Elmer Model 1720-X spectrometer.

3. Results and Discussion

Preparation of Polymer

p -PDAmC_n-PVA was synthesized using 1-chloro-2,4,6-trinitrobenzene as the condensing reagent [12] and the structure was confirmed using NMR spectroscopy, IR spectroscopy, and gel permeation chromatography. The degrees of esterification were 20 ($n = 6$) and 30 mol% ($n = 10$), respectively. The attempt to condense with carbodiimide was unsuccessful.

Photoreaction of p -PDA Diester Solution

The absorption spectrum of p -PDAdiC₁₀ in dichloromethane shows a maximum at 320 nm and the absorption coefficient is $3.37 \times 10^4 M^{-1}cm^{-1}$ (Fig. 1). On irradiation the absorption intensity decreased rapidly during the first 3 s, and then slowly decreased with an appearance of shoulder around 310 nm. This fact suggests the occurrence of *trans*-*cis* isomerization in the solution. After 60 min, the absorption intensity decreased remarkably accompanying the shift of absorption maximum to a shorter wavelength, which was caused by cycloaddition of double bonds in the p -PDAdiC₁₀ solution. The *trans*-*cis* isomerization is much faster than cycloaddition of double bonds so that the isomerization is dominant and reaches photostationary state during the first stage of the irradiation. The formation of cyclobutane ring proceeds slowly during longer term.

Photoreaction of Polymer Solution

The absorption spectrum of p -PDAmC₁₀-PVA in dichloromethane is similar to that of p -PDAdiC₁₀ solution and has a maximum at the same wavelength (Fig. 2). However, the behavior on irradiation is different from that of the diester solution (Fig. 3). The absorption intensity de-

Fig. 1 Absorption spectrum of p -PDAdiC₁₀ in dichloromethane and its change on irradiation.

Fig. 2 Absorption spectrum of p -PDAmC₁₀-PVA in dichloromethane and its change on irradiation.

Fig. 3 Time course of spectral changes in dichloromethane on irradiation.

creased monotonously and the maximum shifted to a shorter wavelength suggesting cycloaddition of double bonds. This result means that cycloaddition proceeds rapidly enough to compete with *trans*-*cis* isomerization. This fact suggests that *p*-PDA chromophores of the polymer exist in association with each other even in the solution, because the *p*-PDA groups are linked each other by the PVA chains and have the tendency to associate each other [14]. The fluorescence spectrum of a *p*-PDAmC₁₀-PVA solution has a maximum at 373 nm with a shoulder peak at 387 nm (Fig. 4). The maximum shifts to a little bit longer wavelength than that of the diester solution (368 nm), and the intensity of the shoulder peak is much larger. This result also indicates that *p*-PDA chromophores of the polymer have interaction and associated each other.

Fig. 4 Fluorescence spectra of PVA-*p*-PDAmC₁₀ and *p*-PDAdiC₁₀ in dichloromethane.

Fig. 5 Absorption spectrum of a PVA-*p*-PDAmC₁₀ film and its change on irradiation.

Photoreaction of Polymer Film

Fig. 5 shows the absorption spectrum of a *p*-PDAmC₁₀-PVA film. The maximum is 306 nm, shorter than that of the polymer solution, and longer than that of the LB film of *p*-PDAmC_n (290 nm) [8]. This implies that orientation of *p*-PDA chromophores is different from that in solution, probably more ordered orientation was achieved. It is interesting to note that the small crystalline islands were observed in the film by a polarizing microscope, and showed phase transition repeatedly on heating cycles. On irradiation the absorption band decreased rapidly and its maximum shifted as same as that in solution. This result indicates that the *p*-PDA chromophores also aggregate in the polymer film. In this case the decrease of double bonds was confirmed by IR spectra. After exposure the film became insoluble in dichloromethane and in tetrahydrofuran.

On summary, *p*-PDA chromophores, which were introduced in polymer system, form the aggregate easily and undergo cycloaddition effectively.

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