PII: S0032-3861(97)00520-X

Polymer Vol. 39 No. 11, pp. 2169-2173, 1998

0032-3861/98/$19.00+0.00

Photochemical behaviour of poly(vinyl alcohol) bearing *p*-phenylenediacrylate groups

Toshiki Komatsu[a,*], Hirochika Sakuragi[b], Jun'ichi Nagasawa[c] and Fusae Nakanishi[c]

[a] *Joint Graduate Course of Chemistry, University of Tsukuba, 1-1 Tennodai, Tsukuba, Ibaraki 305, Japan*

[b] *Department of Chemistry, University of Tsukuba, 1-1 Tennodai, Tsukuba, Ibaraki 305, Japan*

[c] *National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan*

(Received 7 October 1996; revised 3 March 1997; accepted 20 June 1997)

Spectral features and photochemical reactivities were studied on poly(vinyl alcohol) bearing *p*-phenylenediacrylate groups (PVA–*p*-PDAmC$_2$) in comparison with ethyl hydrogen *p*-phenylenediacrylate (*p*-PDAmC$_2$). PVA–*p*-PDAmC$_2$ has a very high photoreactivity compared with *p*-PDAmC$_2$; this can be ascribed to the formation of ground state pairs of *p*-PDAmC$_2$ moieties as side chains due to repulsive interaction between the hydrophobic side chains and the hydrophilic main PVA polymer chain. Some polymers showed features of photoresist with a resolution of 2.5 μm. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: monoethyl ester of *p*-phenylenediacrylic acid; PVA; photoreactions)

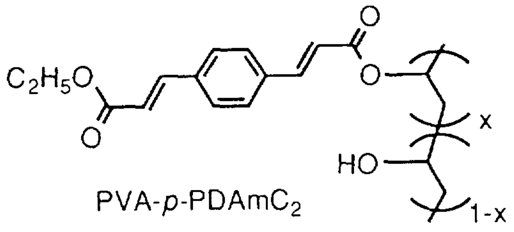
INTRODUCTION

The photochemical reaction, particularly dimerization of C–C double bond takes place not only in solution, but also in a solid state and in a polymer material. Photoinduced dimerization was applied to crosslinking materials, and many studies have been performed from various viewpoints[1].

Some of significant results were reported in the reaction of 2,5-distyrylpyradine (DSP)[2] and styrylpyridinium (SbQ) salt[3,4]. Photopolymerization of DSP in a crystalline state was topochemically controlled by the monomer lattice and gave polymer crystals. This result provided a new aspect in photodimerization of bifunctional substrates. On the other hand, the SbQ salts were utilized to prepare water-soluble polymers combined with poly(vinyl alcohol) (PVA). The polymers exhibited high crosslinkability as well as high water-solubility.

In connection with the above compounds, *p*-phenylenediacrylic acid (*p*-PDA) was designed as another bifunctional substrate to prepare photosensitive polymers[5–8]. The reactions of mono- and di-esters of *p*-PDA were investigated in a solid state and in polymers as well as in solution. In concentrated solutions, the diethyl ester formed ground state aggregates which gave exciplexes on excitation, as revealed by fluorescence spectroscopy[7]. The monoester of *p*-PDA (*p*-PDAmCn) having a long alkyl chain had amphiphilic nature so that the molecules could be arranged side by side to prepare Langmuir-Blodgett multilayers that were photoreactive[9]. Longer alkyl chain monoesters of *p*-PDA were also introduced into PVA and resulting polymers were found to be highly photosensitive[10]. Thus *p*-PDA moiety shows different photoreactivity depending on reaction systems and seems to be one of attractive compounds as photofunctional materials. Actually, some other polymers having *p*-PDA esters provided the excellent photoresist for an argon laser with sensitizers[11].

In this report, investigation has been extended to PVA–*p*-PDAmCn system using shorter alkyl chain monoester of *p*-PDA (ethyl hydrogen *p*-phenylenediacrylate: *p*-PDAmC$_2$) in order to evaluate its photochemical behaviour and to explore possibility to apply as water-soluble photoresist. We have prepared PVA–*p*-PDAmC$_2$ with different content of *p*-PDAmC$_2$ and their photoreactivity was evaluated by spectroscopic methods such as u.v. and fluorescence spectra. Attempt for patterning was also carried out with these polymers.



PVA-*p*-PDAmC$_2$

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA-117; fully saponified; degree of polymerization, 1700) was supplied from Kuraray. Solvents, dichloromethane, chloroform (Merck, spectrograde), 1,2-dichloroethane (Wako, GR), were used as received.

---

* To whom correspondence should be addressed

Preparation of ethyl hydrogen p-phenylenediacrylate (p-PDAmC$_2$)

p-Formylcinnamic acid (20.0 g, 0.12 mol), prepared from the reaction of terephthalaldehyde with malonic acid in acetonitrile containing pyridine[12], was heated to reflux with ethyl iodide (22.4 g, 0.14 mol) in *N,N*-dimethylacetamide (200 ml) in the presence of potassium carbonate (44.5 g, 0.32 mol) for 3 h. After cooling to room temperature, the resulting mixture was poured into water and extracted with diethyl ether. Evaporation of the solvent gave ethyl *p*-formylcinnamate as a yellow oil (23 g, almost quantitative). This product was used for next synthesis without further purification. Crude ethyl *p*-formylcinnamate was purified with crystallization from benzene–hexane; M.p. 41.5–42.5°C; i.r. (KBr) 1700 cm^{-1} ($\nu_{C=O}$), 1638 cm^{-1} ($\nu_{C=C}$), 1604 cm^{-1} ($\nu_{p\text{-}Ph}$). ^{1}H-n.m.r. ($CDCl_3$) 1.36 (*t*, 3H, $J = 7.1$ Hz, CH_3), 4.29 (*q*, 2H, $J = 7.1$ Hz, CH_2), 6.56 (*d*, 1H, = CH–CO), 7.68 (*d*, 2H, Aryl H), 7.72 (*d*, 1H, $J = 16.0$ Hz, ArCH = C), 7.91 (*d*, 2H, $J = 8.3$ Hz, Aryl H), and 10.04 (*s*, 1H, –CHO) ppm. Analysis for $C_{12}H_{12}O_3$: calculated—C, 70.57%; H, 5.92%; found—70.71%; H, 5.92%.

A mixture of malonic acid (18 g, 0.17 mol), ethyl *p*-formylcinnamate (23 g, 0.12 mol), pyridine (70 ml), and piperidine (1 ml) was refluxed for 4 h. After cooling to room temperature, the mixture was poured into water and the resulting precipitate was collected by filtration. The product was purified by recrystallization from methanol (7.2 g, 31% from *p*-formylcinnamic acid); ^{1}H-n.m.r. ($CDCl_3$) 1.35 (*t*, 3H, $J = 7.1$ Hz, CH_3, 4.28 (q, 2H, $J = 7.1$ Hz, CH_2), 6.49 (*d*, 2H, $J = 15.9$ Hz, ArCH = C), 7.57 (*s*, 4H, Aryl H), 7.68 (*d*, 1H, $J = 15.9$ Hz, C = CH–COOEt), 7.77 (*d*, 1H, $J = 15.9$ Hz, C = CH–COOH) ppm; u.v. ($CHCl_3$): 321 nm ($\epsilon 4.8 \times 10^4\ M^{-1}\ cm^{-1}$); i.r. (KBr) 3419 cm^{-1} ($\nu_{O\text{-}H}$), 1676 cm^{-1} ($\nu_{C=O}$), 1631 cm^{-1} ($\nu_{C=C}$). Analysis for $C_{14}H_{14}O_4$: calculated—C, 68.28%; H, 5.73%; found—C, 68.30%; H, 5.70%. *p*-PDAmC$_2$ crystals showed a mesophase between 201.8–215.6°C. This behaviour was confirmed by differential scanning calorimetry measurement and polarizing microscopy.

Preparation of poly(vinyl alcohol) bearing p-phenylenediacrylate groups (PVA–p-PDAmC$_2$)

The procedures were similar to those reported for preparation of poly(vinyloxycarbonylchalcone) by Watanabe *et al.*[13]. As a typical example, PVA–*p*-PDAmC$_2$ with 10–20 mol% esterification degrees was prepared as follows: PVA (1 g) was dissolved in *N,N*-dimethylacetamide (20 ml) by heating. To this solution, after cooling, were added *p*-PDAmC$_2$ (0.56 g), picryl chloride (0.56 g), and pyridine (0.36 g). The mixture was stirred at 80°C for 2–6 h. The reaction mixture was added to methanol (400 ml), and the resulting PVA–*p*-PDAmC$_2$ was repeatedly precipitated from dichloromethane/methanol.

In another case, 5.1 g of PVA was used under otherwise the same conditions for preparation of PVA–*p*-PDAmC$_2$ with a 0.19 mol% esterification degree. PVA–*p*-PDAmC$_2$ with a less than 0.01 mol% esterification degree prepared from 5 g of PVA and 0.28 g of *p*-PDAmC$_2$ together with similar amounts of other materials to the above. The reaction mixture was similarly treated with methanol and the precipitated PVA–*p*-PDAmC$_2$ was purified by repeated precipitations from water/methanol.

The esterification degrees, which corresponded to PDA contents, were calculated from the absorption spectra by using molar absorption coefficients of *p*-PDAmC$_2$ as chromophore; u.v. ($CHCl_3$) 319 nm.

Spectral measurements

Absorption spectra were measured with a Shimadzu UV-160 spectrophotometer. Infrared absorption spectra were measured on a JASCO IR-810 spectrometer.

Fluorescence spectra were measured with a JASCO FP-777 spectrofluorometer. The excitation light was filtered through a Hoya U-340 glass filter and attenuated through a Kenko ND-20S filter if necessary. Fluorescence excitation spectra were measured through a Corning 0-52 glass filter. Sample solutions were magnetically stirred.

Photoreactions

Solutions of *p*-PDAmC$_2$ and PVA–*p*-PDAmC$_2$ in chloroform were placed in a 10 × 10 mm quartz cuvette. The solutions were stirred magnetically and irradiated with 313 nm light isolated from a 500 W super high pressure mercury lamp through an aqueous solution of K_2CrO_4 (0.265 g dm^{-3}) + K_2CO_3 (5.0 g dm^{-3}) and a Hoya U-330 glass filter. The progress of reaction was followed by measuring absorption spectra.

Film preparation

A solution of 10 wt% PVA–*p*-PDAmC$_2$ in 1,2-dichloroethane or water was spin coated on a clean quartz substrate that was processed by treating with acetone, nitric acid, and ozone.

Patterning

Exposure time for PVA–*p*-PDAmC$_2$ films was determined by a gray scale technique. A test pattern for sticky printing from Toppan Printing was used for patterning of PVA–*p*-PDAmC$_2$ films (PDA contents: 0.19 and 20 mol%). Irradiation conditions were similar to those employed for solution samples. Light intensity was 2.54 mW/cm^2 determined by the method of Heller and Langan[14]. Development was carried out in water for a film having 0.19 mol% of PDA groups and in dichloromethane for a film having 20 mol% of PDA groups. After the development, the residual image was examined by an optical microscope (Leica), and the thickness was measured.

RESULTS AND DISCUSSION

Preparation of PVA–p-PDAmC$_2$

Esterification of PVA with *p*-PDAmC$_2$ was performed using picryl chloride as a condensing reagent together with pyridine, as used for esterification with *p*-PDAmC$_6$ and *p*-PDAmC$_{10}$. Picryl chloride was previously employed in preparation of poly(vinyloxycarbonylchalcone) by Watanabe *et al.*[13]. The molar ratio of PVA/*p*-PDAmC$_2$ was changed to control the esterification degree, but the ratio of *p*-PDAmC$_2$, picryl chloride, and pyridine remained nearly constant as described in the Experimental section.

Solubility of PVA–p-PDAmC$_2$

Solubility of PVA–*p*-PDAmC$_2$ depended upon the content of the PDA pendant in the polymer chain. The dependence is shown in *Table 1* by listing the most favourable solvents for the polymers. The solubility in water was changed abruptly between PDA contents of 10 and 1 mol%. PVA–*p*-PDAmC$_2$ with PDA contents of

Table 1 Dependence of solubility of PVA-*p*-PDAmC$_2$ on their PDA content

Molar ratio (*p*-PDAmC$_2$:PVA)	PDA content/mol%	Solvents
1:1	20–10	Benzene, CH$_2$Cl$_2$
1:10	1.0	Water-ethanol (1:1)
1:50	0.19	Water
1:100	< 0.01	Water

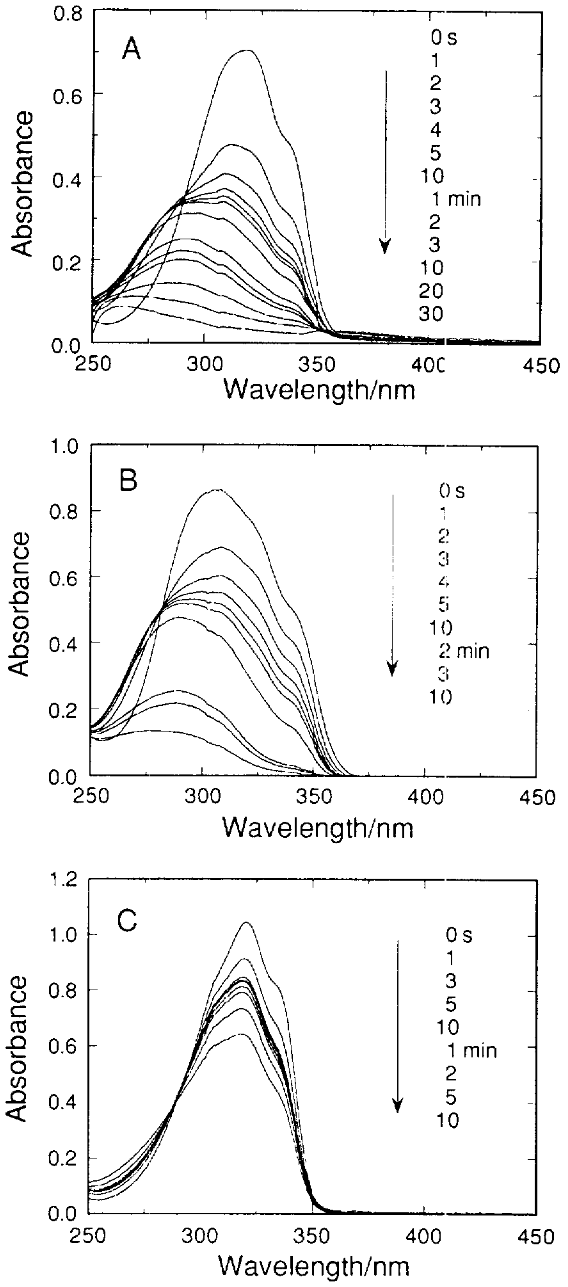


Figure 1 Spectral change on irradiation of PVA-*p*-PDAmC$_2$ with a PDA content of 20 mol% in chloroform (A) and film (B) and of *p*-PDAmC$_2$ in chloroform (C)

10–1 mol% were scarcely soluble in methanol, ethanol, 2-propanol, THF, benzene, dichloromethane, chloroform, acetonitrile, and water, but soluble in water–ethanol (1:1). These results suggest that the molar ratio of the pendant group to the main chain controls hydrophobic/hydrophilic properties of the polymers.

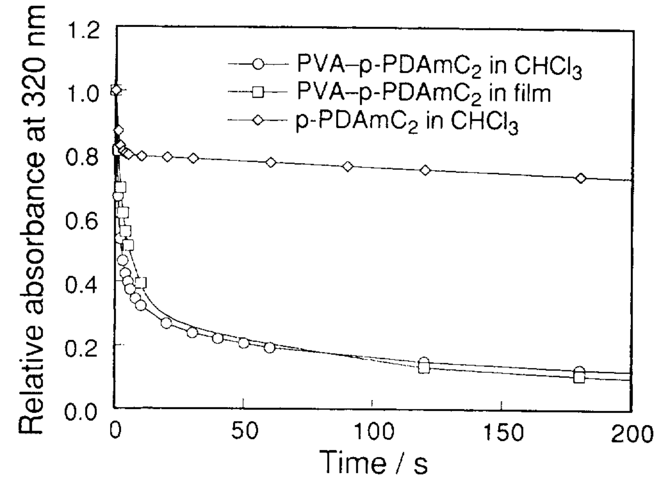


Figure 2 Time profiles of absorption spectra of PVA-*p*-PDAmC$_2$ with a PDA content of 20 mol% and *p*-PDAmC$_2$ monitored at the peak wavelengths of the starting materials

Changes in absorption spectrum upon irradiation

Figure 1 shows absorption spectrum changes observed on irradiation of PVA-*p*-PDAmC$_2$ (PDA content of 20 mol%) in chloroform (*Figure 1A*) and film (*Figure 1B*) and on irradiation of monomeric *p*-PDAmC$_2$ in chloroform (*Figure 1C*). The absorption maximum (λ_{max}) appeared at 321 nm for *p*-PDAmC$_2$ and PVA-*p*-PDAmC$_2$ in solution; however, the maximum shifted to shorter wavelengths for a film of PVA-*p*-PDAmC$_2$. On irradiation with 313 nm light the spectra exerted a remarkable change; PVA-*p*-PDAmC$_2$ showed, in solution as well as in film, a rapid decrease in intensity around the absorption peak involving an increase in shorter wavelengths with an isosbestic point followed by a rather slow decrease with a marked peak shift. In contrast, monomeric *p*-PDAmC$_2$ showed only a rapid process but no spectral shift in solution.

Time profiles of the absorption spectrum monitored at the peak wavelength of the starting materials are shown in *Figure 2*. Comparison of the features of spectral changes between the monomeric and polymeric materials indicates that the rapid changes observed for all three samples are due to decrease of the original conjugate systems, but that the major processes involved are somewhat different. In the monomeric *p*-PDAmC$_2$ isomerization of the double bond may be responsible for this rapid change resulting in a photostationary mixture. In the polymeric PVA-*p*-PDAmC$_2$, however, both isomerization and cycloaddition of the double bonds may contribute to the large decrease in absorbance. Cyclobutane formation in PVA-*p*-PDAmC$_2$ was also suggested by the following analyses: An i.r. band at 1620 cm^{-1} due to the double bond decreased in intensity during irradiation for polymeric materials in a KBr pellet and the peak shifted to shorter wavelength in u.v. spectra.

The above results indicate that photoreactivity of the *p*-PDAmC$_2$ chromophore is increased by being linked to the PVA chain.

Changes in fluorescence spectrum upon irradiation

Figure 3 shows fluorescence and fluorescence excitation spectra of PVA-*p*-PDAmC$_2$ (PDA content of 20 mol%) in chloroform and film. The fluorescence spectrum in solution was composed of roughly two bands around 375 and 450 nm. In a polymer film a broad band was highly predominant around 430 nm and any band was barely

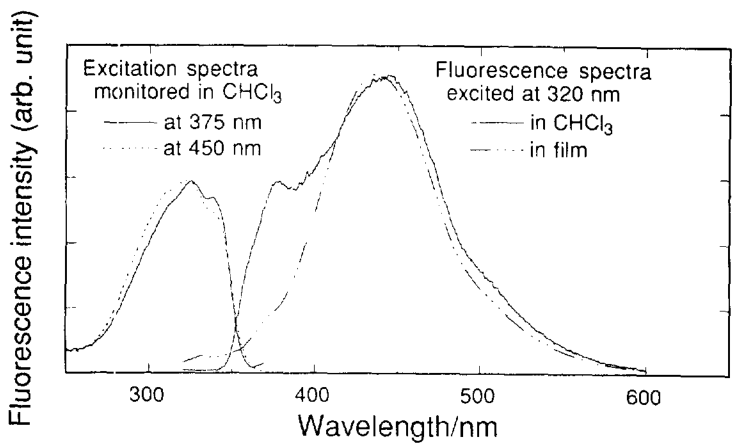


Figure 3 Fluorescence and fluorescence excitation spectra of PVA-*p*-PDAmC$_2$ with a PDA content of 20 mol% in chloroform and film

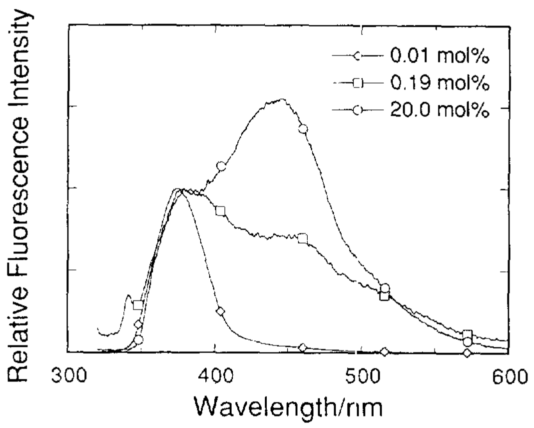


Figure 4 Effects of PDA content on the fluorescence spectrum of PVA-*p*-PDAmC$_2$. The spectra were measured in water, water–ethanol (1:1), and chloroform for PVA-*p*-PDAmC$_2$ with PDA contents of 0.01, 0.19, and 20 mol%, respectively

detected in shorter wavelengths. Monomeric *p*-PDAmC$_2$ exhibited only a shorter wavelength band in dilute solutions. The shorter and longer wavelength bands were identified as the monomer and excimer emissions, respectively. Fluorescence excitation spectra of PVA-*p*-PDAmC$_2$, as monitored at the peak wavelengths at 375 and 450 nm in chloroform, gave slightly different spectra from each other; one at 375 nm was essentially identical with the absorption spectrum of *p*-PDAmC$_2$ in the same solvent (*Figure 1C*), but the other at 450 nm was slightly shifted to shorter wavelengths and almost identical with the absorption spectrum of PVA-*p*-PDAmC$_2$ (*Figure 1A*). These observations indicate that the *p*-PDAmC$_2$ moieties in PVA-*p*-PDAmC$_2$ molecules interact with each other in the ground state and excitation of the chromophore pairs (or aggregates) brings about the excimer emission.

Figure 4 shows fluorescence spectra of three kinds of PVA-*p*-PDAmC$_2$ with different PDA contents in chloroform. PVA-*p*-PDAmC$_2$ (PDA content of 0.01 mol%) exhibited only a shorter wavelength band similar to that from the monomeric *p*-PDAmC$_2$; however, a broad longer wavelength band grew with the increase in the PDA content. This broad band could be ascribed to excimers between the pendant PDA moieties by comparison of its band shape and position with those of the fluorescence spectra in solution. As shown in *Figure 5*, PVA-*p*-PDAmC$_2$ (PDA content of 20 mol%) exerted a remarkable decrease in fluorescence intensity with excitation light of spectrofluorometer during measurements of the spectrum in chloroform and film, particularly in the longer wavelength band due to the excimer, remaining the shorter wavelength band due to the monomeric *p*-PDAmC$_2$. These observations indicate that the prominent photoreactivity of PVA-*p*-PDAmC$_2$ arise from interactions between the *p*-PDAmC$_2$ chromophores.

PVA having pendant hexyl and decyl *p*-PDA moieties, PVA-*p*-PDAmC$_6$ and PVA-*p*-PDAmC$_{10}$, respectively, were previously studied[10].* The absorption and fluorescence behavir of PVA-*p*-PDAmC$_{10}$ are very similar to that of the present PVA-*p*-PDAmC$_2$.

It was previously reported that a polyester of *p*-PDA[15] as well as diethyl *p*-phenylenediacrylate (*p*-PDAdC$_2$)[7] exhibited excimer fluorescence due to excitation of ground state interacting PDA pairs in solution. This is also the case for the PVA-*p*-PDAmC$_2$ system, though the repulsive interaction between the hydrophilic PVA polymer chain and hydrophobic pendant chromophores may play an important role in the formation of the ground state chromophore pairs. Thus, introduction of the *p*-PDAmC$_2$ moieties into the PVA chain increases the probability of interaction between the chromophores leading to isomerization and cycloaddition of the double bonds through excimers. Collapse of the excimer may result, in competition with the cycloaddition, in efficient formation of the triplet state of the conjugated double bond, which subsequently isomerizes to the cis geometry[16,17].

Attempted patterning

On the basis of the aforementioned results on the reactivity and solubility of polymers, their applicability to photoresist was examined. For films with a lower PDA content (0.19 mol%) the exposure time and the washing time with water were limited to 2 min, respectively; longer washing times resulted in no print left on the surface. The thickness of films prepared by the spin coating technique was nearly 1.5 μm. With careful conditioning of an exposed polymer film with a PDA content of 0.19 mol%, a pattern was left on the surface of substrate, but the height of remaining pattern was only 51 nm from the surface, i.e. nearly 98% of the film was dissolved in water in comparison

---

* The wavelength of an excimer emission for PVA-*p*-PDAmC$_{10}$ was erroneously reported previously

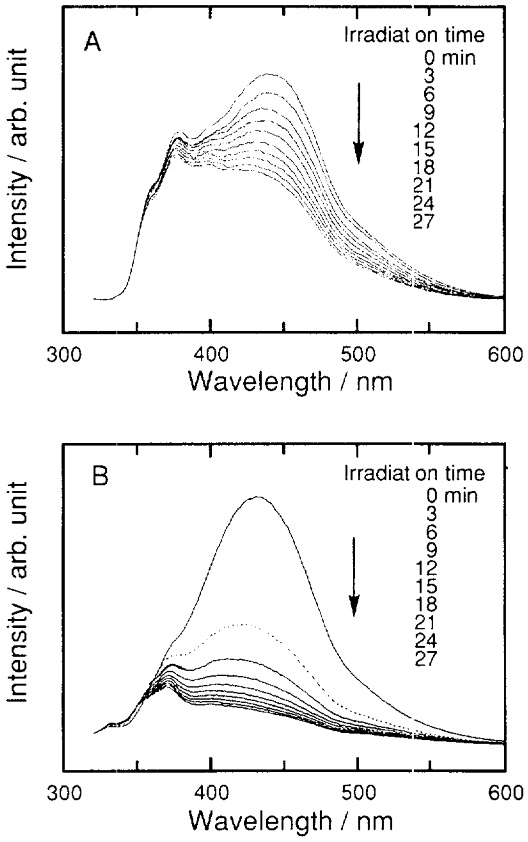


Figure 5 Fluorescence spectral changes for PVA-*p*-PDAmC$_2$ with a PDA content of 20 mol% during the measurements in chloroform (A) and film (B). Each measurement was performed at 3 minutes interval with 305 nm excitation light

with the initial thickness. The bottom of a valley of the pattern was 14 nm from the surface; unexposed parts of the film could not be completely removed.

The film with a higher PDA content (20 mol%) was exposed only for one second to 313 nm light isolated from a 500 W super high pressure mercury lamp through a filter solution to achieve a negative-type photopatterning and washed with dichloromethane for 5 min to leave a print with a resolution of 2.5 μm (*Figure 6*). Exposed areas remained to a significant extent with a fair contrast. This material is of potential value for practical applications though halogenated alkanes should be better replaced by a suitable solvent for development.

CONCLUSIONS

PVAs containing ethyl *p*-PDA moieties with different content have been prepared and their properties such as solubility, photoreactivity have been evaluated. PVA–*p*-PDAmC$_2$ with *p*-PDA content of 20 mol% exhibited a higher photoreactivity than monomeric *p*-PDAmC$_2$ due to the formation of excimers resulting in isomerization and cycloaddition of double bonds in solution and film. The polymers esterified at a more than 10 mol% degree could be used as a photoresist with resolution of 2.5 μm.

Figure 6 An optical micrograph of a negative image of a PVA–*p*-PDAmC$_2$ film contact-printed. The *p*-PDAmC$_2$ content is 20 mol%. The widths of lines and spaces of the mask are 2.78 (No. 2) and 2.48 μm (No. 3), respectively

REFERENCES

1. Saigo, J., *Journal of Synthetic and Organic Chemistry, Japan*, 1989, **47**, 1006, and references cited therein.
2. Hasegawa, M., *Advances in Polymer Science*, 1982, **42**, 1.
3. Ichimura, K., *Makromol. Chem.*, 1987, **188**, 763.
4. Ichimura, K., *Makromol. Chem.*, 1987, **188**, 2973.
5. Cohen, M.D. and Schmidt, G.M., *Journal of the Chemical Society*, 1996, **1964**.
6. Nakanishi, H., Nakanishi, F., Suzuki, Y. and Hasegawa, M., *Journal of Polymer Science: Polymer Chemistry Edition*, 1973, **11**, 2501.
7. Sakamoto, M., Huy, S., Nakanishi, H., Nakanishi, F., Yurugi, T. and Hasegawa, M., *Chemistry Letters*, **1981**, 99.
8. Suzuki, F., Suzuki, Y., Nakanishi, H. and Hasegawa, M., *Journal of Polymer Science, Part A-1*, 1969, **7**, 2319.
9. Nakanishi, F., Okada, S. and Nakanishi, H., *Polymer*, 1989, **30**, 1959.
10. Nagasawa, J., Bhatnagar, R. and Nakanishi, F., *Journal of Photopolymer Science Technology*, 1993, **6**, 139.
11. Ichimura, K. and Nishio, Y., *Journal of Polymer Science: Polymer Chemistry Edition*, 1987, **25**, 1579.
12. Wiley, R.H. and Hobson, P.H., *Journal of the American Chemical Society*, 1949, **71**, 2429.
13. Watanabe, S., Harashima, S. and Tsukada, N., *Polymer Journal of Science, Part A: Polymer Chemistry Edition*, 1986, **24**, 1227.
14. Heller, H.G. and Langan, J.R., *Journal of the Chemical Society, Perkin Trans.*, 1981, **2**, 341.
15. Graley, M., Reiser, A., Roberts, A.J. and Phillips, D., *Macromolecules*, 1981, **14**, 1752.
16. Caldwell, R.A. and Creed, D., *Acc. Chemistry Research*, 1980, **13**, 45.
17. Itoh, H., Senda, Y., Sakuragi, H. and Tokumaru, K., *Bulletin of the Chemical Society of Japan*, 1993, **66**, 1312.