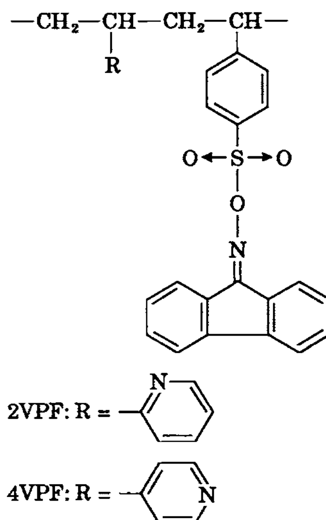
Photoinduced Change in Dissolution of Polyvinylpyridine Bearing Imino Sulfonate Units

INTRODUCTION

The preparation of polymers which become soluble in solvent on irradiation with light is important because of their application to positive-type photoresists. To accomplish the photoinduced dissolution of polymers, many methods have been studied. They can be classified into two categories, i.e., photochemically induced depolymerization of polymers and photochemical formation of polar groups in the polymer chain or polymer matrix. The depolymerizations of polycarbonate[1,2] and polyaldehyde[3] by strong acids formed photochemically have been studied by several workers. This system has the property of self-development since the volatile monomer is liberated. The photoinduced formation of polar groups such as phenol,[4-6] carboxylic acid,[7-10] and sulfonic acid[5,11,12] has been devised to dissolve polymers in aqueous alkaline solutions. In the previous paper[13] we reported that poly[2-(dialkylamino)ethyl methacrylate] bearing imino sulfonate units became soluble in slightly basic aqueous solution on irradiation with UV light. Here we report the photoinduced change in dissolution of copolymers of vinylpyridine and 9-fluorenylideneimino *p*-styrenesulfonate, which forms sulfonic acid on irradiation with UV light.



EXPERIMENTAL

Materials

The preparation of 9-fluorenilideneimino *p*-styrenesulfonate (FISS) was reported elsewhere.[12] 2-Vinylpyridine (2-VP) and 4-vinylpyridine (4-VP) were of reagent grade and used after distillation under reduced pressure. Polymers were prepared by the radical copolymerization of FISS and 2-VP or 4-VP at 55°C for 6 h *in vacuo* using AIBN as initiator. *N,N*-dimethylformamide (DMF) was used as solvent. All polymers were purified by dissolving in chloroform and precipitating with hexane or diethyl ether. The purification procedure was repeated until no absorption due to FISS could be detected in the precipitating solvent. The copolymerization and purification were carried out in darkness to prevent the decomposition of FISS units by daylight. Detailed polymerization conditions and characteristics of the polymers are shown in Table I. The FISS fraction in copolymers was determined from the absorbance at 300 nm in $CHCl_3$ (ϵ = 1.12 × 10^4 1/mol cm). Although

Journal of Applied Polymer Science, Vol. 41, 2527-2532 (1990)
© 1990 John Wiley & Sons, Inc. CCC 0021-8995/90/9-102527-06$04.00

TABLE I
Preparation Conditions and Characteristics of Polymers[a]

Polymer	2VP (g)	4VP (g)	FISS (g)	DMF (mL)	Yield (%)	η_{sp}/C[b] (dL/g)	FISS content in polymer (mol %)
2VPF (7)	1.27	—	0.23	2.1	12	0.18	7.1
2VPF (9)	1.09	—	0.41	1.9	4	0.30	9.0
2VPF (23)	0.81	—	0.69	1.4	7	0.13	22.6
4VPF (8)	—	2.38	0.62	7.9	9	0.27	7.6

[a] Concentration of initiator AIBN is 0.05 mol/L.
[b] [C] = 0.5 g/dL, solvent; chloroform, at 30°C.

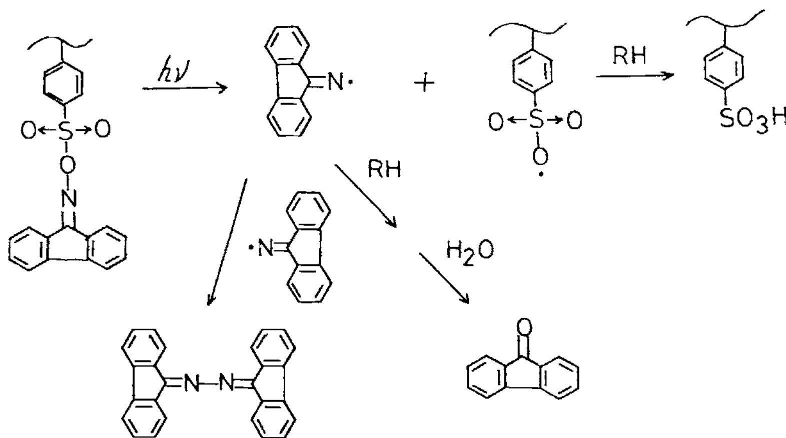
esters of sulfonic acid are generally unstable in basic media, no decomposition of FISS was observed during the polymerization and purification procedures.

Measurements

The dissolved fraction of polymers was measured as follows. A chloroform solution of polymers was coated on a quartz plate (1 × 4 × 0.1 cm) and dried. The thickness of polymer film on the quartz plate measured by surface profilometer was 0.4 μm. The absorbance of sample films at 313 nm was always below 2.0. The fraction of dissolved polymer was calculated from the difference between absorbance at 254 nm of the sample on the quartz plate before and after dipping the quartz plate with the sample film in the developer for a given time at room temperature. Irradiation of polymers was carried out with a high-pressure mercury lamp (Toshiba SHL-100UV, 75 W) at a distance of 9 cm in air. A glass filter (Toshiba UV-29) was used to absorb light of shorter wavelength than 300 nm.

RESULTS AND DISCUSSION

FISS units showed λ_{max} at 254 nm ($\epsilon = 6.76 \times 10^4$ 1/mol cm in CH_2Cl_2) and its shoulder peaks at wavelength around 300 ($\epsilon = 1.12 \times 10^4$ 1/mol cm in CH_2Cl_2) and 360 nm ($\epsilon = 3.98 \times 10^2$ 1/mol cm in CH_2Cl_2). The absorption band of imino sulfonate compounds depends on the structure of imino moieties. The imino sulfonate compounds are generally synthesized from sulfonyl chloride and oxime which can be derived from ketones. Thus it is easy to synthesize imino sulfonate compounds showing the proper region of light absorption. On irradiation with UV light, the cleavage of —O—N— bonds of FISS, and the subsequent abstraction of hydrogen atoms from residual solvent in the polymer film or polymer molecules, lead to the formation of sulfonic acid accompanying the formation of fluorenone azine and/or fluorenone as shown in Scheme 1:



Scheme 1

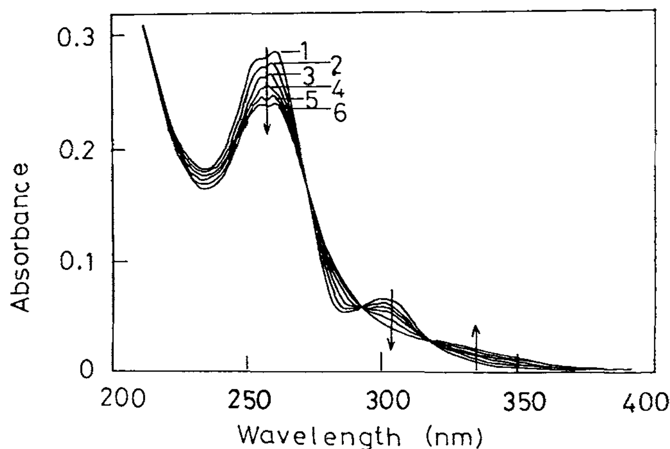


Fig. 1. Spectral change of 2VPF(9) film on irradiation with UV light in air at room temperature. Irradiation time (min): (1) 0; (2) 0.5; (3) 1; (4) 2; (5) 4; (6) 8. The arrows show the direction of change in absorbance with irradiation.

A representative change in absorption spectrum of polymers bearing imino sulfonate groups on irradiation is shown in Figure 1. The absorbance at 254 and 300 nm decreased with irradiation time. The absorption around 340 nm increased slightly with irradiation time, which is due to the formation of fluorenone azine.

Figure 2 shows plots of fraction of photolyzed FISS units of the polymers against irradiation time. The FISS fraction in polymers and polymer structure of the base polymer did not significantly affect the rate of photolysis of FISS units. The same phenomenon has been observed for the copolymer of 2-(dialkylamino)ethyl methacrylate and FISS.[13] Furthermore, the quantum yield Φ of photolysis of FISS units incorporated in poly[2-(dimethylamino)ethyl methacrylate] has been reported to be 0.46.[13]

Figure 3 shows the relationship between dissolved fraction of copolymers of FISS and 2-VP in a methanol–water mixture (3 : 1, v/v) as developer and irradiation time. Although 2VPF(9) and

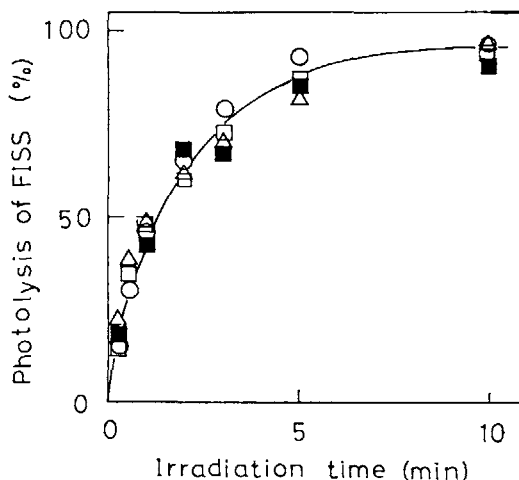


Fig. 2. Relationship between fraction of FISS photolyzed and irradiation time. Polymer: (△) 2VPF(7); (○) 2VPF(9); (□) 2VPF(23); (■) 4VPF(8).

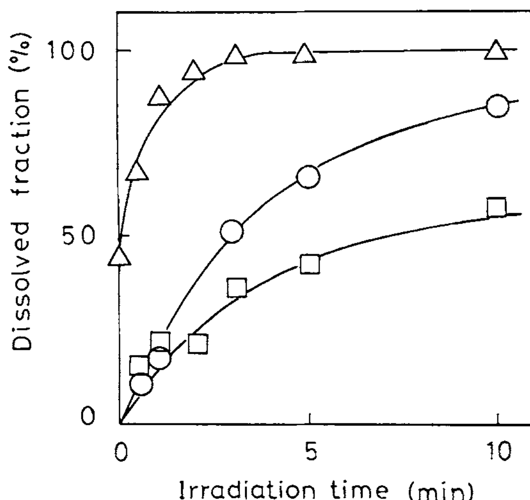


Fig. 3. Relationship between dissolved fraction of 2VPF and irradiation time. Development was carried out with a methanol-water mixture (3 : 1, v/v) for 5 min at room temperature. Polymer: (△) 2VPF(7); (○) 2VPF(9); (□) 2VPF(23).

2VPF(23) did not dissolve in the developer, 2VPF(7) partially dissolved in the developer. The dissolved fraction of the polymers increased with irradiation time and the dissolution occurred parallel to the photolysis of FISS units of the polymers. Thus the polymers have the properties of positive-type photoresist. Neutralization of sulfonic acid formed on exposure to pyridinium moieties can form ampholytic polymers, which shows good solubility in the aqueous developer. The dissolved fraction of the polymers after irradiation for 10 min decreased in the order 2VPF(7) > 2VPF(9) > 2VPF(23). The photolysis of FISS units accompanies the formation of fluorenone and/or fluorenone azine which are less soluble in the developer. They may interfere with the dissolution of the irradiated polymer in the developer. It was reported that a polymer which is soluble in a developer can be protected from dissolution by a blended compound insoluble in the devel-

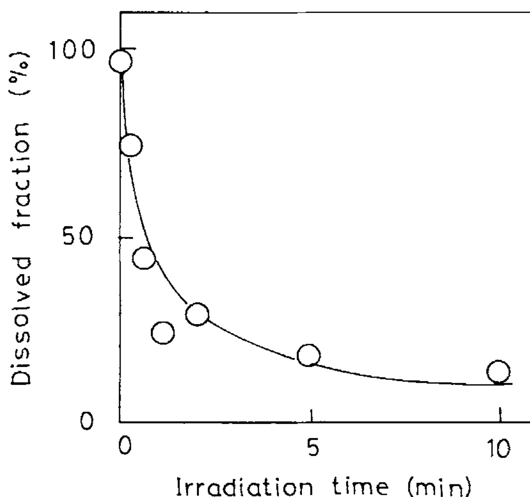


Fig. 4. Relationship between dissolved fraction of 4VPF(8) and irradiation time. Development was carried out with methanol for 1 min at room temperature.

oper.[7-10] Thus 2VPF(23) whose fraction of FISS units is high showed lower dissolved fraction than that of 2VPF(7) and 2VPF(9) on irradiation with UV light. It is important to control the fraction of FISS units to get polymers which show good dissolution properties as positive-type photoresist.

Figure 4 shows the relationship between dissolved fraction of 4VPF(8) and irradiation time. Although 4VPF(8) dissolved in methanol and partially dissolved in a methanol–water mixture (3 : 1, v/v), it became insoluble in the solvents on irradiation with UV light. The irradiated 4VPF(8) did not dissolve even in solvent-containing salts like NaCl. The insolubilization occurred parallel to the photolysis of FISS units. Thus the polymer has the properties of negative-type photoresist. The 4-pyridinium and styrenesulfonate moieties of exposed 4VPF(8) may form tight ion pair complexes as observed for the polyion complexes between poly(*N*-alkyl-4-vinylpyridinium) and poly(styrenesulfonate).[14] On the other hand, 2-pyridinium and styrenesulfonate moieties of the exposed 2VPF may not form tight ion pair complexes because of steric factors. It is well known that the nitrogen atom of poly(2-vinylpyridine) is protected from chemical reactions because of the steric hindrance of the polymer backbone. Thus the exposed 2VPF had a character of ampholytic properties soluble in aqueous methanol as developer.

References

1. J. M. J. Frechet, F. Bouchard, F. M. Houlihan, B. Kryczka, E. Eichier, N. Clecak, and C. G. Willson, *J. Imaging Sci.*, **30**, 59 (1986).

2. J. M. J. Frechet, F. Bouchard, E. Eichler, F. M. Houlihan, T. Iizawa, B. Kryczka, and C. G. Willson, *Polym. J.*, **19**, 31 (1987).

3. H. Ito and C. G. Willson, *Polym. Eng. Sci.*, **23**, 1013 (1983).

4. H. Ito, C. G. Willson, J. M. J. Frechet, M. J. Farrall, and E. Eichler, *Macromolecules*, **16**, 510 (1983).

5. F. M. Houlihan, A. Shugard, R. Gooden, and E. Reichmanis, *Macromolecules*, **21**, 2001 (1988).

6. J. M. J. Frecht, T. G. Tessier, C. G. Willson, and H. Ito, *Macromolecules*, **18**, 317 (1985).

7. C. W. Wilkins, Jr., E. Reichmanis, and E. A. Chandross, *J. Electrochem. Soc.*, **129**, 2552 (1982).

8. E. Reichmanis, C. W. Wilkins, Jr., D. A. Price, and E. A. Chandross, *J. Electrochem. Soc.*, **130**, 1433 (1983).

9. E. Reichmanis, R. Gooden, C. W. Wilkins, Jr., and H. Schonhorn, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 1075 (1983).

10. E. Reichmanis, B. C. Smith, G. Smolinsky, and C. W. Wilkins, Jr., *J. Electrochem. Soc.*, **134**, 653 (1987).

11. M. Shirai, N. Katsuta, M. Tsunooka, M. Tanaka, K. Nishijima, and K. Ishikawa, *Chem. Express*, **3**, 439 (1988).

12. M. Shirai, M. Tsunooka, M. Tanaka, K. Nishijima, and K. Ishikawa, *J. Polym. Sci. Polym. Chem., Ed.*, **27**, 325 (1989).

13. M. Shirai, N. Katsuta, M. Tsunooka, M. Tanaka, and K. Nishijima, *Makromol. Chem.*, **190**, 2099 (1989).

14. E. Tsuchida, Y. Osada, and K. Sanada, *J. Polym. Sci.*, **10**, 3397 (1972).

MASAMITSU SHIRAI*
TAKAYUKI SAITO
MASAHIRO TSUNOOKA
MAKOTO TANAKA

Department of Applied Chemistry
Faculty of Engineering
University of Osaka Prefecture
Sakai, Osaka 591, Japan

* To whom correspondence should be addressed.

KANJI NISHIJIMA

Nippon Paint Co. Ltd.
19–17 Ikedanaka-Machi
Neyagawa, Osaka 572, Japan

Received January 25, 1989
Accepted February 15, 1990