Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Snyder, D. M.(1989) 'Solid-State Photoquaternization of Polymer-Bound Pyridine', Journal of Macromolecular Science, Part A, 26: 10, 1437 — 1450

To link to this Article: DOI: 10.1080/00222338908052061

URL: http://dx.doi.org/10.1080/00222338908052061

J. MACROMOL. SCI.–CHEM., A26(10), pp. 1437-1450 (1989)

SOLID-STATE PHOTOQUATERNIZATION OF POLYMER-BOUND PYRIDINE

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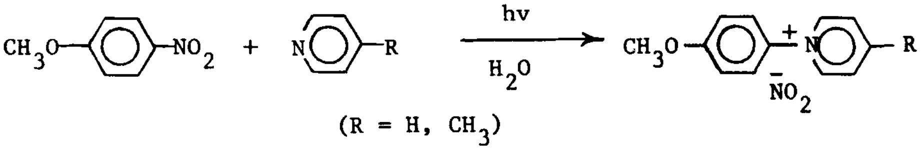
ABSTRACT

A study of the solid-state ultraviolet photoreaction of polymer-bound pyridine and *p*-nitrophenoxy groups has shown that pyridinium nitrite crosslinks result from the photoquaternization process. The generation of ionic groups in the crosslinking effectively inhibits the solubility of the irradiated polymer matrix in nonpolar solvents.

INTRODUCTION

One of the primary limitations of conventional negative-acting photoresist materials is that the photochemically crosslinked matrix, while insolubilized relative to the unexposed polymer, still retains an appreciable affinity for solvent and will tend to swell during development. As a result, such systems are not applicable to photolithography requiring submicron resolution [1, 2]. Novel chemical approaches to circumvent this problem have centered on altering the polarity of the exposed polymer to decrease its solvent affinity. Deprotection of poly(*p*-*t*-butoxycarbonyloxystyrene) to poly(vinylphenol) with photogenerated acid catalysts [3] and formation of ion pairs by photolytic redox reaction of polymer-bound tetrathiafulvalene-tetrabromomethane charge-transfer complexes [4, 5] have been used to increase the polarity of the irradiated polymer matrix and to decrease its solubility in nonpolar solvents.



SCHEME 1.

We envisioned an alternate approach as a system that would crosslink the polymer photochemically and form an ionic matrix in the same reaction, i.e., a photo-driven process that would simultaneously form a covalent bond and a fully developed ionic charge from neutral precursors. Because generation of ionic species from neutral reactants is well known in the conversion of tertiary amines to quaternary ammonium salts, we examined the known photochemistry of nitrogen compounds.

A candidate reaction was found in the work of Letsinger et al. [6] who reported the photochemical conversion of an aqueous *t*-butanol solution of 4-methylpyridine and *p*-nitroanisole to the corresponding pyridinium nitrite salt, as shown in Scheme 1.

The report was particularly interesting in that it was noted that the reaction would take place even when a dilute solution was frozen to dry-ice temperature. The quantum yield (ϕ) at 335 nm for the solution-phase reaction was in the 0.01 to 0.02 range, depending on pyridine concentration. However, at very large excess it dropped to 0.0076 [7], which was interpreted as evidence that the excited-state nitroaromatic was being quenched by pyridine in competition with the substitution. A recent report on photochemical displacement of nitrite ion from 1-methoxy-4-nitronaphthalene with aliphatic amines rather than pyridine, also supports the initial conclusion that the process is an S_N2 Ar* reaction that proceeds through the triplet excited state of the nitroaromatic compounds [8]. Despite the relatively low quantum yield, the overall reaction was reported to be quite clean and preparative runs of several hours yielded the pyridinium nitrite as the sole product. On this basis, a test polymer was synthesized to determine if the photoquaternization would take place in a solid-state matrix.

EXPERIMENTAL

Measurements

IR spectra were recorded on a Perkin Elmer 1750 Fourier-transform spectrometer, using either KBr pellets or thin films cast from THF on salt plates.

^1H-NMR spectra were recorded on a JEOL FX-900, with $CDCl_3$ as solvent, and are reported in δ (ppm) relative to $(CH_3)_4Si$ internal standard with coupling constants (J) reported in Hz. T_g measurements were done with a Perkin-Elmer DSC-4 differential scanning calorimeter. Ultraviolet/visible spectra were recorded on a Perkin-Elmer 552 UV/Vis spectrophotometer with 1 cm cells. GPC measurements were done on a Waters Associates ALC 202/401 liquid chromatograph with Microstyragel columns eluted with THF and a refractive index detector at room temperature. The % insolubles vs. wavelength exposure testing was done with an Oriel Corporation 6181 500-W high-pressure Hg arc lamp, equipped with a double diffraction grating monochromator, a G190 power supply, and a Gralab 605 electronic shutter control. The % NO_2^- vs exposure time testing was done in a Ray-O-Net photochemical reactor equipped with a rotating carousel rack and 254-nm lamps. Photon fluxes were determined either by potassium ferrioxalate actinometry [10] or through use of an IL390 "Light Bug" ultraviolet photometer from International Light, Inc. All solvents and reagents, with the exception of chloromethylstyrene from Polysciences Inc., were reagent-grade materials from Aldrich Chemical Company and were used as received. Elemental analyses were done by Galbraith Laboratories of Knoxville, Tennessee.

Preparation of *p*-(4-Nitrophenoxymethyl)styrene (*5*)

Chloromethylstyrene (*3*) (15.2 g, 0.10 mol of a 40:60 mol:mol mixture of para:ortho isomers) and tetra-*n*-butylammonium *p*-nitrophenoxide (*4*) (38.0 g, 0.10 mol, prepared by reaction of tetra-*n*-butylammonium hydroxide and *p*-nitrophenol in CH_3OH followed by solvent removal) in 150 mL $CHCl_3$ were heated with stirring under N_2 to 55-60°C for 6 h. The mixture was stripped of solvent *in vacuo*, taken up in ethyl ether, washed with water, and dried over $MgSO_4$. Suction filtration and solvent removal gave 25.1 g of a pale yellow oil which was chromatographed on silica gel with 1.5:1 hexane/EtOAc to isolate 10.7 g of predominantly para isomer. The solvent-stripped fraction crystallized slowly at room temperature and was recrystallized from 50 mL cyclohexane to give 7.50 g of white solid *5* with mp 66-68°C. ^1H NMR 5.13 (2H, s), 5.29 (1H, d, J = 10.7), 5.76 (1H, d, J = 16.9), 6.81 (1H, d, d, J = 8.5, 10.8), 7.29 (2H, d, J = 9.4), 7.40 (4H, m), 8.21 (2H, m). IR (KBr): 1590, 1500, 1340, 1260, 1100, 1000, 920, 895 cm^{-1}.

Preparation of Terpolymer

Styrene (*1*) (3.12 g, 0.03 mol), 4-vinylpyridine (*2*) (1.05 g, 0.01 mol), and *p*-(nitrophenoxy)methylstyrene (*5*) (2.55 g, 0.01 mol) were combined in 6.0

mL dry benzene with 0.36 g (0.0015 mol) benzoyl peroxide and purged with N_2 vigorously before placing in a 70°C water bath for 3 h. The crude polymer solution was precipitated into 200 mL CH_3OH and the solvent removed under vacuum to give 4.42 g of pale-orange, amorphous, transparent solid. IR (thin film on NaCl plate): 1595, 1510, 1390, 1260, 1110, 1000, 845 cm^{-1}.

Preparation of Copolymers

Both test copolymers were prepared and isolated by the same procedure as the terpolymer. (a) 3.15 g of amorphous solid *8* was prepared from styrene (*1*) (3.12 g, 0.03 mol) and 4-vinylpyridine (*2*) (1.05 g, 0.01 mol) in 6.0 mL dry benzene with 0.29 g benzoyl peroxide at 70°C for 3 h. (b) 0.57 g of amorphous solid *9* was prepared from *1* (0.86 g, 0.008 mol) and *p*-nitrophenoxy)methylstyrene (*5*) (0.70 g, 0.0027 mol) in 2 mL dry benzene with 0.08 g benzoyl peroxide at 70°C for 3 h. IR for *8* (thin film on NaCl plate): 1770, 1600, 1495, 1455, 1418, 1225, 1070, 1000 cm^{-1}. IR for *9* (thin film on NaCl plate): 1590, 1520, 1450, 1340, 1260, 1175, 1110, 849 cm^{-1}.

Wavelength vs % Film Insolubility Testing

A sufficient volume of 10 wt% solution of the terpolymer in THF to just cover the entire surface was applied to glass microscope slide covers 18 X 18 mm in size (Fisher Scientific, thickness #1), and the solvent was evaporated under ambient conditions. After vacuum treatment to insure complete solvent removal, the plates were individually reweighed and positioned in the output beam of a double diffraction grating monochromator for exposure to selected wavelengths of the Hg arc lamp for 5, 15, 30, 60, and 120 min. Each plate was developed by soaking in CH_2Cl_2 for 30 s and drying under vacuum. Reweighing determined the amount of insoluble film remaining. The potassium ferrioxalate-derived photon flux per unit area in the beam for each wavelength was used to evaluate the total incident energy for each sample. The values were then normalized for sample weight variation.

Exposure Energy vs Nitrite Content and Film Insolubles Testing

Standard 75 X 25 mm glass microscope slides were coated with the 10 wt% terpolymer solution in THF on one side to a final thickness (after vacuum drying) of 1-1.3 μm. A set of three plates was sealed inside Vycor glass tubes, flushed with N_2, and placed on the carousel rack in the well of the Ray-O-Net photochemical reactor to be irradiated with the 254-nm lamps for 5, 15, 30, 45, and 60 min. The exposed polymer was removed from the surface as a powder, weighed, and shaken with 4 mL of 0.01 *M* NaCl for 4 h (no apparent increase in NO_2^- content was found for a given sample after 2 h, but the ion-exchange time was doubled to insure as complete a removal as possible). The extract was filtered, a 3-mL aliquot was combined with the Greiss reagents, and the absorbance of the solution was measured after 30 min on the UV spectrophotometer at 535 nm vs $NaNO_2$ solution calibration standards. In the exposure time vs film insolubility testing, the irradiated polymer was likewise removed as a powder, weighed, extracted with 7 mL CH_2Cl_2, and vacuum-dried. Then the insoluble residue was determined by reweighing. The 254-nm photon flux/cm^2 in the reactor was determined with the IL-390 ultraviolet photometer.

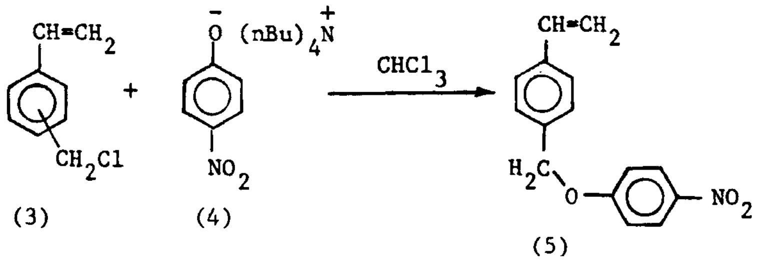
CAS REGISTRY NUMBERS

Registry No. *1*, 100-42-5; *2*, 75944-25-1; *3*, 72923-40-1 (para), 22570-84-9 (ortho); *6*, 100-17-4; *7*, 536-75-4; *p*-nitrophenol, 100-02-7; tetrabutylammonium hydroxide, 2052-49-5.

RESULTS AND DISCUSSION

Monomers used for the synthesis of the test polymer were commercially available styrene (*1*) and 4-vinylpyridine (*2*), while the *p*-nitrophenoxy-containing monomer (*5*) was prepared from commercial chloromethylstyrene (*3*) as shown in Scheme 2.

The crude monomer from Scheme 2 could be purified by chromatography

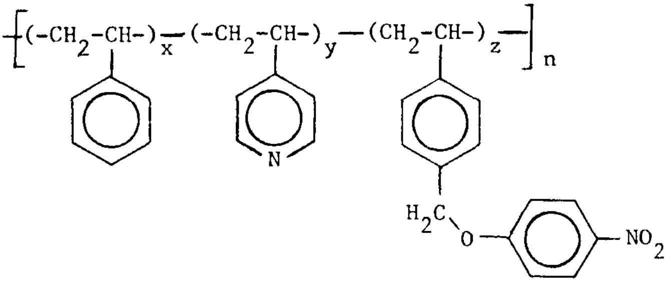


SCHEME 2.

TABLE 1. Elemental Analysis of Terpolymer[a] vs Monomer Incorporation

	Calculated from feed ratio ($x = 3, y = 1, z = 1$)	Actual analysis	Calculated best-fit values ($x = 0.66, y = 0.48, z = 1$)
%C	82.11	75.41	76.6
%H	6.59	6.10	5.8
%N	4.16	5.55	5.4
%O	7.13	12.82	12.8

[a]Terpolymer structure:



and recrystallization from cyclohexane to isolate pure *p*-(nitrophenoxy)-methylstyrene (*5*) as a stable white solid.

The terpolymer was prepared by combining a 3:1:1 mole ratio of styrene (*1*), 4-vinylpyridine (*2*) and *p*-(4-nitrophenoxy)methylstyrene (*5*) in benzene and polymerizing with benzoyl peroxide. The resulting amorphous, glassy solid was freely soluble in benzene, CH_2Cl_2, $CHCl_3$, and THF and showed an IR spectrum (thin film) consistent with the presence of the nitroaromatic and the pyridine groups. GPC data of the precipitated polymer showed a $\bar{M}_w$ of 10 091 and $\bar{M}_n$ of 5302, i.e., a polydispersity of 1.903. DSC measurement located the T_g at approximately 55°C. Elemental analysis indicated that the mole ratio of incorporated monomers was substantially different from the initial synthesis ratio. Calculations that isolated the contribution to the elemental analysis results of the nitrogen and nitrogen-oxygen containing monomers indicated that the final incorporation ratio was actually closer to 0.66:0.48:1 (Table 1). This gives a ratio of pyridine to nitrophenoxy reactive sites in the polymer as approximately 1:2.

Samples of the polymer were cast as thin films on glass from a 10-wt%

TABLE 2. Terpolymer Photoresponse vs Wavelength

Wavelength, nm	$E_{1/2}$,[a] kJ/g
254	10.3
313	60.9
366	154.2

[a] $E_{1/2}$ energy required to insolubilize 50% of the film sample by using CH_2Cl_2 development.

solution in THF for irradiation testing, and exposure to ultraviolet resulted in insolubilization of the polymer with the degree of reaction directly related to exposure time. The same photoresponse was observed when the polymer film was irradiated either in air or under N_2. While it has been reported that the solution-phase photoquaternization was run with UV light of wavelength of 298 nm, our study indicated that the crosslinking reaction appeared to proceed most efficiently at 254 nm, as measured by the % insolubilization on a total incident-energy basis. In these experiments the film samples were exposed through a double diffraction grating monochromator to select only the wavelengths of maximum output from the Hg arc lamp. Actinometry-derived photon fluxes at each wavelength were used to calculate total incident energy, and these data were correlated with film insolubilization for each exposure time. Linear regression analysis of the data was used to compare the polymer photoresponse at each wavelength by using an arbitrarily defined point on the plots (Table 2). On this basis it can be seen that the polymer crosslinking is considerably more efficient at 254 nm, requiring approximately 6 to 15 times more energy to reach equivalent degrees of insolubilization ($E_{1/2}$) at 313 and 366 nm, respectively.

Spectroscopic Study of Pyridine Photoquaternization

Comparison of spectral changes in the components of the solution-phase photoquaternization with the corresponding polymer photoreaction showed striking similarities. UV absorbance spectra were run on dilute CH_3CN solutions of both 4-ethylpyridine (*7*) and *p*-nitroanisole (*6*), and these solutions were then irradiated individually with 254-nm light for up to 180 min. During this time, *p*-nitroanisole showed only a slight photodecomposition while 4-ethylpyridine was unaffected. An equimolar mixture of the two components showed an additive UV spectrum, but in a mixture with a large excess of 4-ethylpyridine, the UV spectrum was altered by shifting of the strong $-NO_2$ band from 280 to 300 nm with an accompanying significant reduction in intensity (Fig. 1).

It was suggested in Letsinger's work [6] that a complex of pyridine and the nitroaromatic compound might be involved in the photoquaternization, and the CH_3CN solution phase spectra tend to support this hypothesis. The spectral perturbation of the $-NO_2$ band only with large excess of pyridine suggests a complex with a relatively low association constant, which also would be consistent with the low quantum yield for the overall process. Photolysis of the excess pyridine solution at 254 nm showed a sharp decrease in the absorbance of the shifted $-NO_2$ band and the gradual appearance of a broad band at 410 nm (Fig. 2). A thin film of the terpolymer showed a UV spectrum in which the nitroaromatic $-NO_2$ band was shifted even further toward 330 nm, and irradiation of this sample gave comparable changes with a rapid decrease in the intensity of the $-NO_2$ band and the gradual appearance of the broad 405-410 nm band (Fig. 3).

Analysis of Nitrite Ion Formation

The spectral similarities to the solution-phase reaction did not discount the possibility that the crosslinking responsible for polymer insolubilization might be due to some unanticipated photoreaction involving only one of the reactive sites. To resolve this question, two additional polymers were prepared, incorporating only one of the reactive sites in each. Copolymers of (*1*) with (*2*) (Copolymer *8*) and (*1*) with (*5*) (Copolymer *9*) were synthesized by the same procedure and characterized by their spectra. Irradiation of thin-film samples of each copolymer at 254 nm showed negligible photoresponse under standard conditions, which were sufficient to insolubilize >50% of the bifunctional terpolymer.

As additional evidence that the photoquaternization process is responsible for the crosslinking, the irradiated terpolymer was analyzed for the presence of nitrite ion. The procedure was based on the Greiss test [9], which is specific for nitrite ion to levels as low as 5×10^{-5} μg of NO_2^- in 0.5 mm^3 of solution. Irradiated film samples of the terpolymer were powdered and soaked for several hours in dilute NaCl solution to ion exchange the nitrite from the polymer matrix. The aqueous solution was then treated with the Greiss reagents to develop a characteristic red-purple color, positively identifying the presence of nitrite ion. A nonexposed control gave completely negative results with the Greiss test procedure. The strong absorbance of the red-purple azo dye at 530-535 nm allowed accurate spectrophotometric determination of NO_2^- content vs irradiation time and % film insolubilization (Table 3).

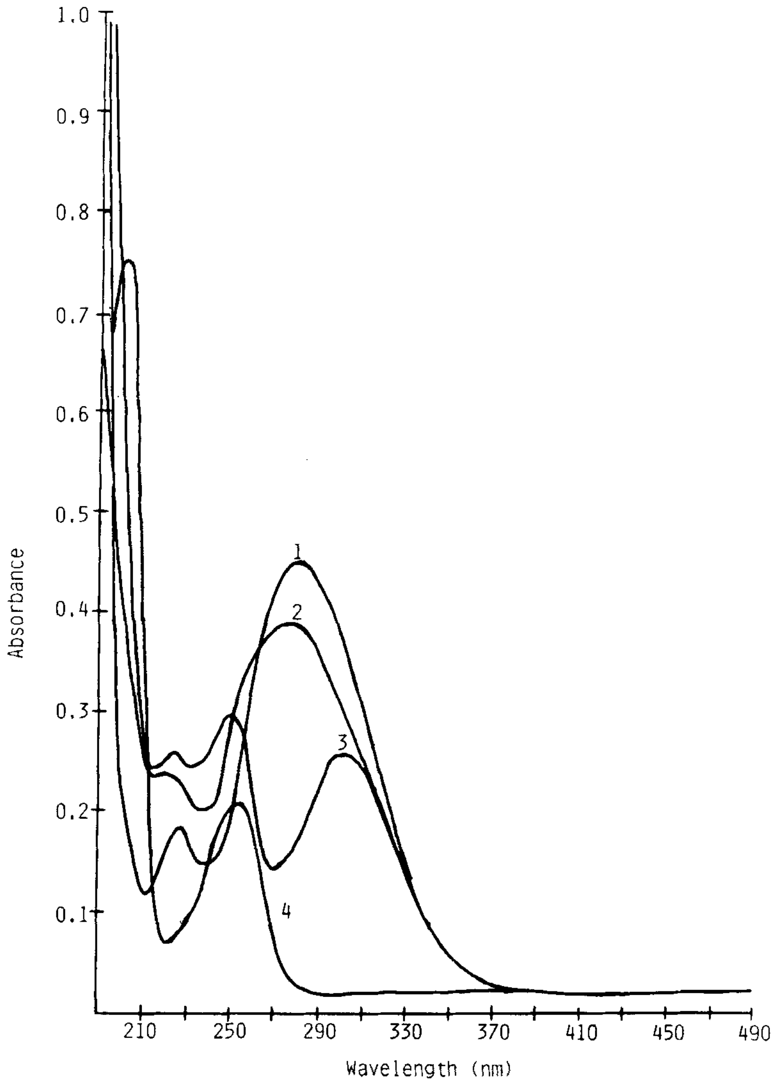


FIG. 1. UV spectra of *p*-nitroanisole (*6*) and 4-ethylpyridine (*7*) in CH_3CN. Curve 1: 20.5 μmol/L 6. Curve 2: 19.5 μmol/L 6 plus 19.5 μmol/L 7. Curve 3: 20.5 μmol/L 6 plus 137 μmol/L 7. Curve 4: 101 μmol/L 7.

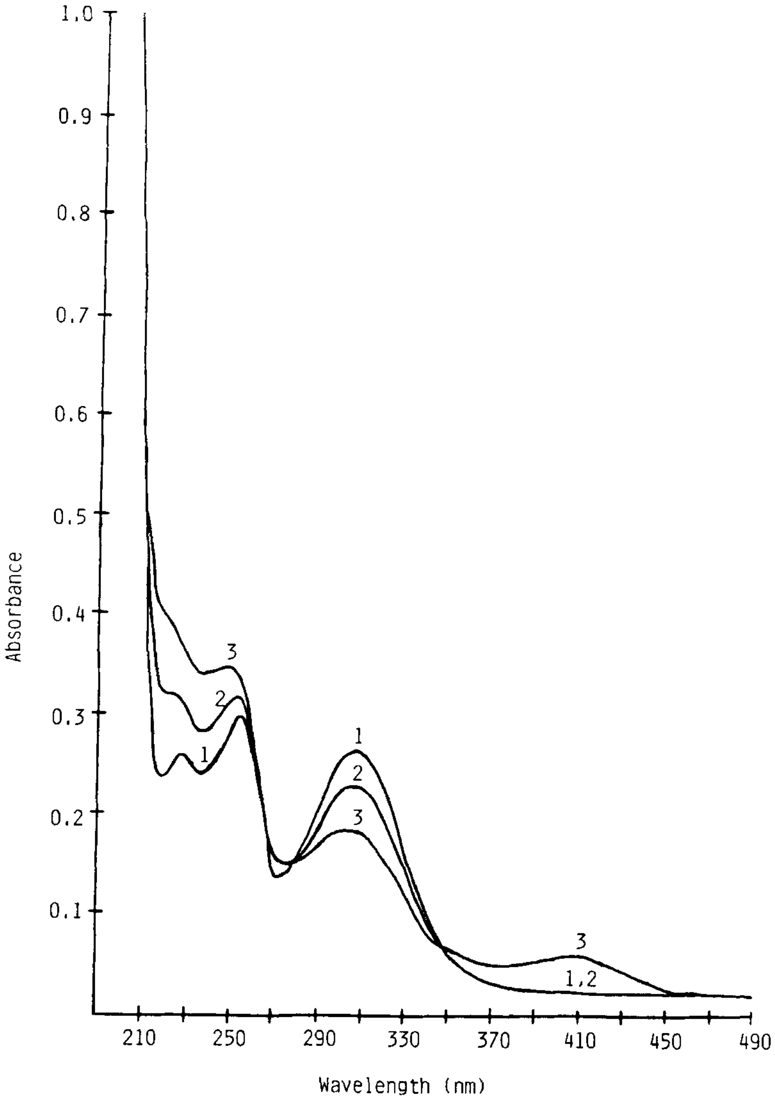


FIG. 2. UV spectra of 254-nm irradiated *p*-nitroanisole (*6*) and 4-ethylpyridine (*7*) in CH_3CN vs exposure time. Curve 1: Initial. Curve 2: 60 min. Curve 3: 180 min. Concentrations: 20.5 μmol/L 6 plus 137 μmol/L 7.

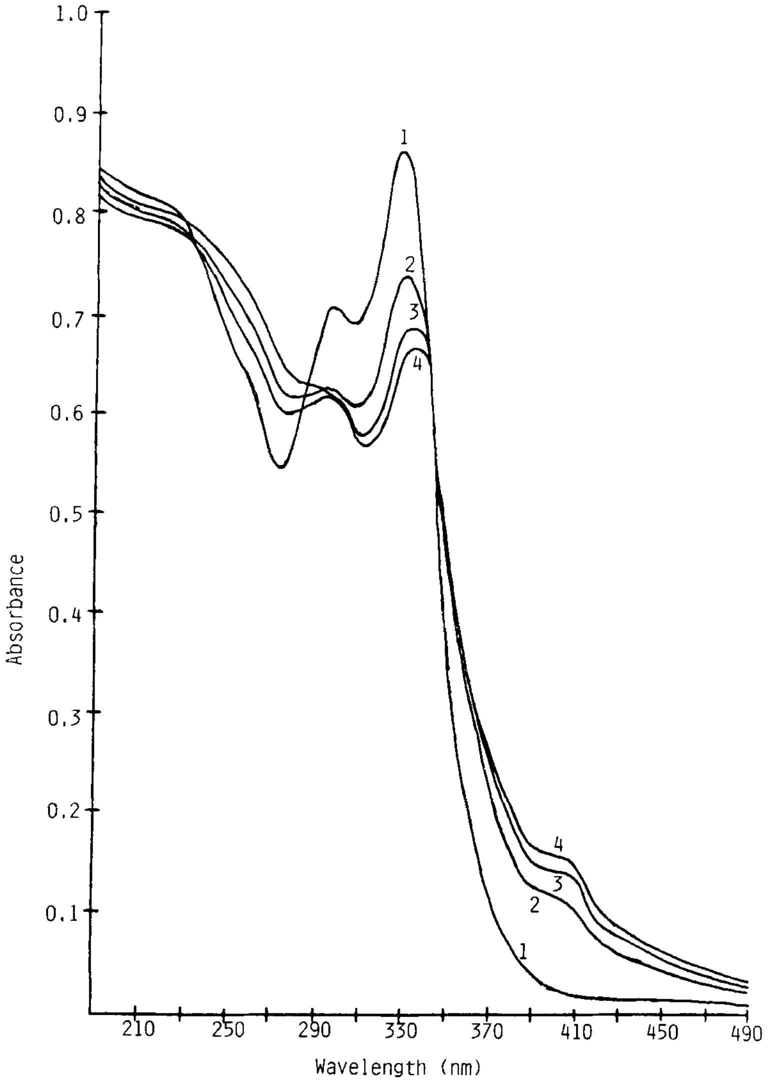


FIG. 3. UV spectrum of 254-nm irradiated terpolymer (thin film on quartz glass) vs exposure time. Curve 1: Initial. Curve 2: 30 min. Curve 3: 60 min. Curve 4: 90 min.

TABLE 3. Terpolymer Photoresponse at 254 nm from NO_2^- Analysis

Exposure, s	254-nm Photons, mol	NO_2^-, mol	Conversion,[a] %	Insoluble, %
450	3.15×10^{-5}	3.08×10^{-8}	0.29	12.0
900	6.37×10^{-5}	4.40×10^{-8}	0.41	33.3
1800	1.27×10^{-4}	5.12×10^{-8}	0.48	34.5
2700	1.91×10^{-4}	5.56×10^{-8}	0.52	46.1
3600	2.55×10^{-4}	6.89×10^{-8}	0.64	54.1

[a] (Moles NO_2^- analyzed/moles theoretical pyridine in irradiated film) × 100.

The data and calculation results show a direct correlation between conversion (as measured by NO_2^- content) and film insolubility. Given the restricted mobility of the reactive sites in the polymer matrix, the decrease in 254 nm quantum yield with conversion from 9.7×10^{-3} at 0.287% conversion to 2.7×10^{-3} at 0.643% is also consistent. Considering the rather modest $\bar{M}_n$ of only 5302 for the polymer, it appears that relatively low degrees of photoquaternization-derived crosslinking are required to affect the solubility of the irradiated film significantly.

CONCLUSIONS

The results of this study have confirmed that the solid-state ultraviolet photoreaction of polymer-bound pyridine and *p*-nitrophenoxy groups results in the formation of pyridinium nitrite crosslinks via photoquaternization. The ionic crosslinking effectively inhibits the solubility of the irradiated polymer matrix in nonpolar solvents although the quantum yield for the process is too low for this test polymer to represent a practical photoresist material. The low quantum yield for the process is most likely the result of a combination of restricted mobility of reactive groups in the solid state and enhanced competitive quenching of the nitrophenoxy excited state relative to substitution.

ACKNOWLEDGMENTS

The author is grateful for the expert assistance of R. A. Shoemaker (GPC analysis), A. G. Geigley (NMR spectra), G. F. Slotter (preparation of Greiss reagents, and B. L. Buckwalter (IR spectra), and to X. T. Phan for helpful discussions.

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Received September 19, 1988
Revision received October 24, 1988