Photochemistry of Polymeric Systems. IV. Photocrosslinking of Copolymers Including Pyridinium Dicyanomethylide Groups

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Synopsis

Photocrosslinkable polymers were obtained by reacting tetracyanoethylene oxide with pyridine units of suitable copolymer. Copolymers of styrene and 4-vinylpyridine dicyanomethylide were synthetized and studied. The methods used for characterization of photocrosslinked films were a "photoresist test" or the measurement of the insolubilization ratio. The reaction is favored by triplet-state sensitizers such as Michler's ketone. The photosensitivity of the copolymers was determined as a function of the wavelength of the radiation used.

INTRODUCTION

Azides are commonly used as photoreticulating agents of polymers.[1] By irradiation they are converted to nitrene. When they are formed in the singlet state, they can be inserted into C—H bonds. When they are generated in the triplet state, they abstrat hydrogens leading to radicals. In both singlet and triplet states, they can add to double bonds. All these processes initiate reticulation of a polymer.[2]

We recently pointed out that the oxygen species obtained by photocleavage of the N-oxide bond of molecules such as pyridine N-oxide or quinoleine N-oxide included in the chain of a polymeric material can also initiate its photoreticulation.[3] In another article we reported the photocleavage of yluric bonds of pyridinium dicyanomethylide brings to dicyanocarbene.[4]

The aim of the present report was to elucidate whether the formation of carbene in a polymeric film will also lead to its photoreticulation. For this purpose we synthetized a series of copolymers containing pyridinium dicyanomethylide units. We studied the behavior of films of these copolymers under irradiation by using the "photoresist test."[3] The variation of the rate of insolubilization and IR and UV spectra of the films were determined as a function of the irradiation time.

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EXPERIMENTAL

Monomers

4-Vinylpyridine (4VP), styrene (St), and methyl methacrylate (MMA) were Merck compounds, p-vinylbenzophenone (VBP) was synthesized by pyrolysis of the corresponding polymer obtained by Friedel–Crafts benzoylation of polystyrene as previously reported.[5]

All monomers were distilled just before use in order to remove polymerization inhibitors.

Copolymers

Nonylided Samples

Copolymers of 4VP with St, MMA, and VBP were obtained by using conventional radical polyaddition. The monomers were dissolved in the appropriate solvent along with α,α'-azobisisobutyronitrile used as the polymerization initiator. The solutions were degassed three times and the vessels were sealed. All samples were polymerized at 60°C and then precipitated in a convenient nonsolvent.[3]

Ylidation of Copolymers

The method described by Linn et al.[6] was followed. A solution of copolymer (2 g in 100 ml tetrahydrofuran, THF) was cooled in an ice bath, and a solution of tetracyanoethylene oxide (1 mole for 1 mole 4VP), freshly prepared, in 50 ml THF was added dropwise with stirring over 1 hr. The mixture was heated at 40°C and stirred for 4 hr under gentle reflux and nitrogen flow. The solution became yellow rapidly during this time and was then precipitated slowly by pouring in petroleum ether. A second dissolution in chloroform and precipitation was carried out, and the purified polymer was filtered and dried under vacuum. The percentage of pyridinium dicyanomethylide groups obtained in the chain was lower than 15% (mol. fr.) (more the copolymer precipitated in bulk):
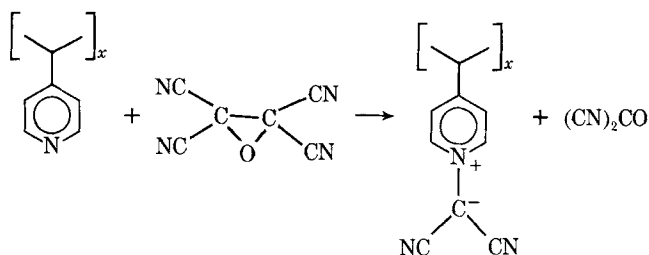
Analytic Characterization

DMF was used as the solvent at 27°C for viscometric measurements. The specific viscosity η_{sp} was determined for solutions at a concentration of 1 g/100 ml before quaternization reactions and is reported in Table I.

TABLE I
Photosensitivity of Different Copolymers Measured by "Photoresist Test" [a]

Sample	Composition	η_{sp}, ml/g	% ylid	S_1, J^{-1} cm^2	S_2, J^{-1} cm^2
1	4VP/ST (6.2–93.8%)	31	6.1	0.06	0.018
2	4VP/ST (10.0–90.0%)	32	9.7	0.10	0.037
3	4VP/ST (14.6–85.4%)	31	13.8	0.20	0.126
3'	4VP/ST (14.6–85.4%)	31	0	0.003	—
4	4VP/MMA (12.6–87.4%)	67	12.0	0.10	0.025
5	4VP/ST/VBP (6.9–90.2%–2.9%)	34	6.8	0.25	0.045

[a] Development solvent: chloroform; S_1 is the photosensitivity without any filter; S_2 the photosensitivity with a glass filter (thickness 1 mm); source: SP 500 Philips lamp; η_{sp} determined before quaternization.

Determination of Pyridinyl and Benzophenone Groups

Before their N-ylidation a conductimetric titration of pyridine groups in copolymers was carried out, choosing the same experimental conditions as those used by Tamikado[7] for his potentiometric determination of pyridine units in 4-vinylpyridine copolymers. A Tacussel CM 05 conductimetry cell was used associated with a Wayne-Kerr B 641 "autobalance universal bridge." The determination of p-vinylbenzophenone units was carried out from UV spectra at 290 nm ($\epsilon = 5880$ l./mole cm).

Determination of N-Ylided Groups

The quantitative determination of N-ylided groups was made by ultraviolet spectrophotometry. We chose ethyl-4-pyridinium dicyanomethylide for a comparative study by recording UV spectra in chloroform. The absorption spectra were recorded in this solvent, and the optical density at 410 nm was used for the determination of N-ylide groups of all copolymers.

Spectroscopic Characterization of Copolymers

IR and UV spectra of polymeric materials were recorded using Beckman IR 18 and Beckman DB.G spectrometers, respectively.

Photoreticulation Tests

Different light sources were used in this study: A Philips SP 500 medium pressure mercury source and a xenon Osram XBO 900 lamp coupled with a GM 250 Schoeffel monochromator.

The determination of the illumination of the exposition light source was measured by a Kipp and Zonen thermopile. The photosensitivity S of the polymeric material can be defined as[2,8]

$$S = K/E = K/It$$

where E is the energy needed to insolubilize 1 cm^2 of the film, I is the illumination determined, t is the time needed for insolubilization, and K is a constant arbitrarily chosen ($K = 1$).

The polymeric materials to be tested were laid out on a polyester film (coated

by vacuum evaporation with a metallic bismuth) using a Braive "filmographe." The thickness of the photosensitive film, after evaporation, was approximately 1 μm. The determination of the irradiation time needed for insolubilization of the samples was made using a so-called "photoresist test" described in a previous article.[3] An alternative method of studying the photoreticulation of a polymeric material is to determine its insolubilization ratio, defined for a given irradiation time as the ratio of the amount m_i insolubilized through reticulation v_s the weight m_0 of the starting sample:

$$\tau_i = (m_i/m_0) \times 100$$

After irradiation the film was put in a solvent for the starting polymer. The insoluble gel was filtered on a crucible (porosity No. 4), washed, dried, and weighed.

Study of Photoreticulation

All irradiations were performed with a mercury medium-pressure source. As seen in Table I, two different sensitivities can be determined depending on the irradiation wavelength range. S_1 is the photosensitivity measured without any filter, and S_2 is the photosensitivity determined with a 1-mm-thick glass filter eliminating UV radiations to 300 nm with a SP 500 Philips source.

The examination of Table I shows that both S_1 and S_2 sensitivity increase with the percent of ylid groups in a given series of copolymers (samples 1, 2, and 3). Moreover, the nonylided sample exhibits very poor sensitivity as expected (sample 3'). S_2 is always lower than S_1; however, rather good photosensitivity is available when the ylidation reaches approximately 15%, as in sample 3. Thus, using this copolymer with irradiation through a glass plate is possible. A comparison between the values of S_1 for samples 2 and 4 points out that the photosensitivity as determined in the "photoresist test" does not depend on the chemical nature of the parent copolymer when the ylidation percent is the same. The adhesive properties of samples 2 and 4 on bismuth films seem to be very similar.

Insolubilization Rate

Figure 1 shows the variation of insolubilization rate versus irradiation time for the three copolymers (samples 1, 2, and 3) by the gravimetric method. For a given irradiation time, the insolubilization rate increases with the percentage of the pyridinium dicyanomethylide groups in the chain, in good agreement with the results of Table I. The initial rates of insolubilization are similar for the three samples.

UV and IR Spectrophotometric Studies

Figure 2 shows the variation of the UV spectrum of a film of copolymer as a function of irradiation time. The 410-nm absorption band corresponding to the ylid bond disappears as the reticulation proceeds. For this reason, thick polymeric films can be photoreticulated by irradiation in the 410-nm range, the optical density of the film decreasing proportionally to the photoreticulation
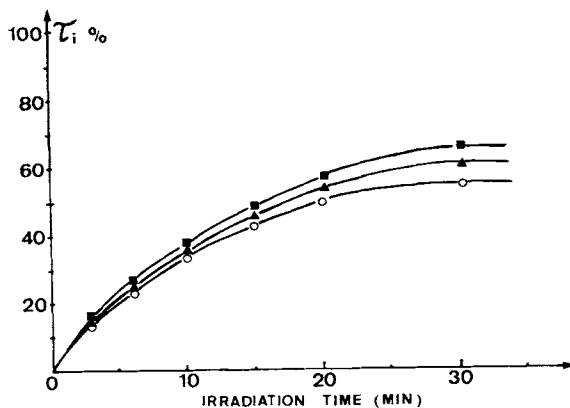
Fig. 1. Variation of the insolubilization ratio in weight of 10-μ films of different copolymers vs. irradiation time with a Philips SP 500 medium-pressure mercury lamp without filter: (O) sample 1; (▲) sample 2; (■) sample 3; $I = 0.2$ W/cm^2

extent. Figure 3 points out that the variation of optical density versus irradiation time is the same for films of different copolymers in which the percentage of pyridine N-dicyanomethylide groups is low as long as their optical density is the same before irradiation.

Figure 4 shows IR spectra of a typical copolymer (sample 2) before and after irradiation. The ylide bands at 1460, 1260, and 830 cm^{-1} no longer exist in the spectrum of the irradiated sample. The first step of the photoreaction is certainly the cleavage of the ylid step of the ylid bond leading to the formation of a very reactive dicyanocarbene. This carbene would be able to extract hydrogen from the polymeric skeleton, and the radicals so created on the polymeric chains would produce the photoreaction through classical recombination reactions. This mechanism is confirmed by the spectra of irradiated copolymers in which the peaks corresponding to 4-vinylpyridine units clearly appear. However, the band corresponding to CN groups disappears completely in the spectra of irra-
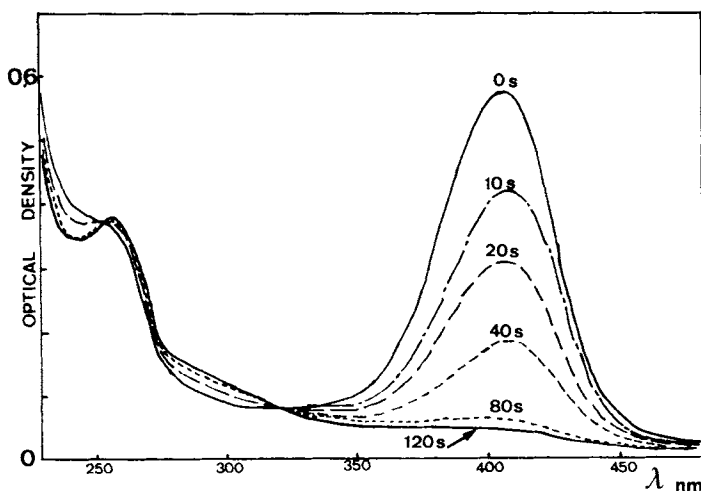

Fig. 2. Variation in UV spectra of film as function of irradiation time (sample 2); $I = 0.2$ W/cm^2
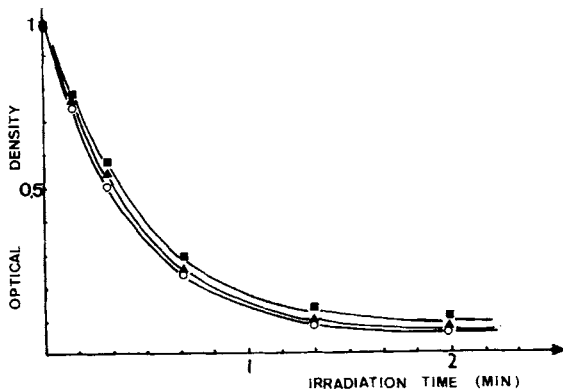
Fig. 3. Variation in optical density at 410 nm of copolymers films having optical density of 1 vs. irradiation time: (O) sample 1; (▲) sample 2; (■) sample 3; I = 0.2 W/cm^2

diated materials. This is curious but does not necessarily mean that this functional group has been eliminated, for instance, via a volatile compound. Actually, this band is very difficult to observe in many cases.

Moreover, a band at 1700 cm^{-1} appears on spectra of irradiated polymers. It probably corresponds to carbonyl groups due to oxidation of the radicals originating from carbene species.
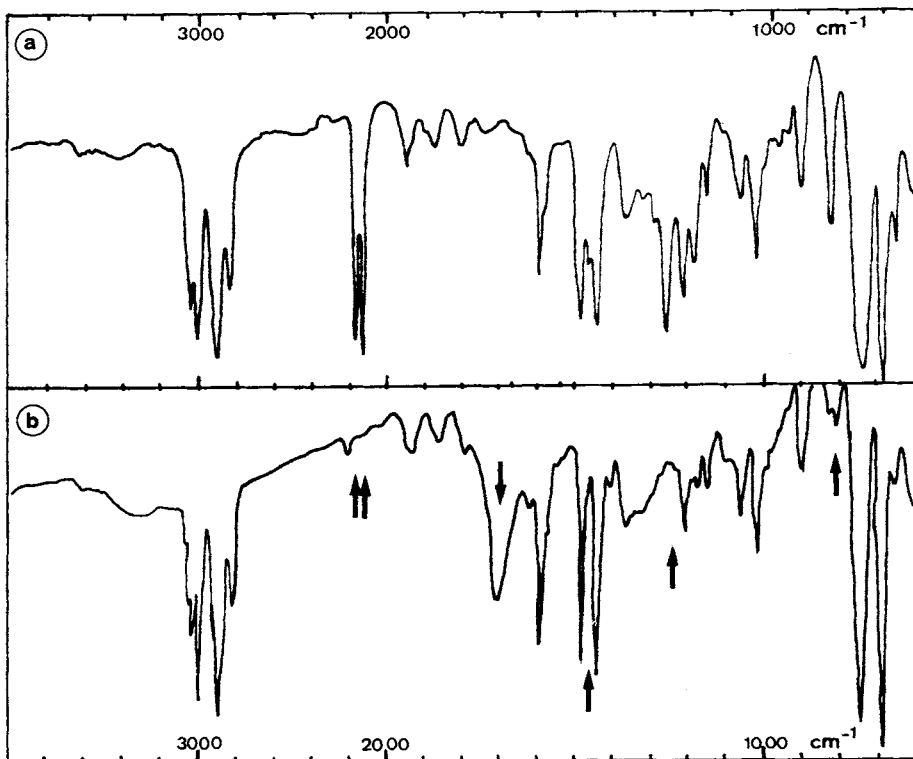

Fig. 4. Comparison of IR spectra of sample 2 film before (a) and after irradiation (b).

Photosensitization

The photocleavage of the ylid N^+—N^- bond of N-aminopyridinium ylids[9] and that of the N^+—O^- bond of pyridine N-oxide as well[10] is a triplet excited-state photoreaction. If excited in the singlet state, these compounds give rise to photoisomerization reactions.

In general, carbenes can be formed either from the singlet state or from the triplet state of their precursors.[11] To date, no study of the photocleavage of dicyanomethylene–pyridinium ylide in polymers has been published. It was interesting to study the action of known photosensitizers in order to elucidate the photocleavage mechanism of these N^+—C^- bonds.

The first photosensitizer studied was Michler's ketone.[12] A 1-μ-thick film was made for photoresist tests with a mixture of copolymer 3 and 10% by weight of Michler's ketone. The UV spectrum of such a mixture in $CHCl_3$ is given in Figure 5. The film was irradiated in the wavelength range of 350 ± 10 nm, near the absorption maximum of Michler's ketone. The measured photosensitivity $S_1 = 0.476$ J^{-1} cm^2 can be compared with $S_1 = 0.20$ in the absence of photosensitizer.

A second test was made from a terpolymer 4VP/ST/VBP (sample 5 of Table I). Its photosensitivity is approximately four times that of sample 1, which contains the same percentage of ylid group. 2.9% benzophenone included in the polymeric skeleton has a higher effect than 10% Michler's ketone added in the bulk.

These data establish clearly that the photosensitivity to insolubilization of the N^+—C^- groups studied is enhanced by addition of a triplet–triplet photosensitizer. The mechanism would be similar for N^+—N^-, N^+—O^-, and N^+—C^- photocleavage. In the present case the energy needed to break N^+—C^- bond is lower than 61 kcal/mole.
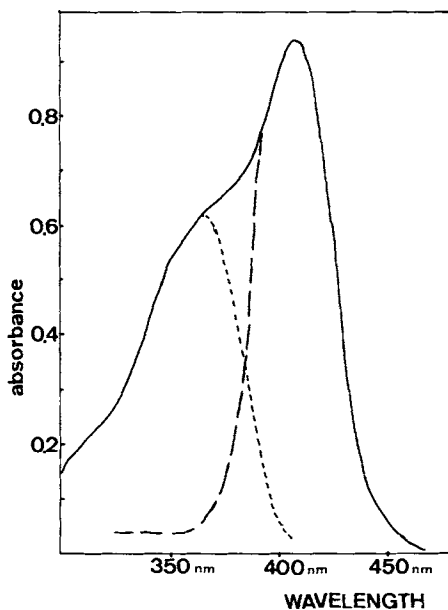

Fig. 5. UV spectra: (—) sample 3 (25 mg/100 cc $CHCl_3$) with 10% of sensitizer (Michler's ketone); (– –) sample 3 only; (- - -) sensitizer.
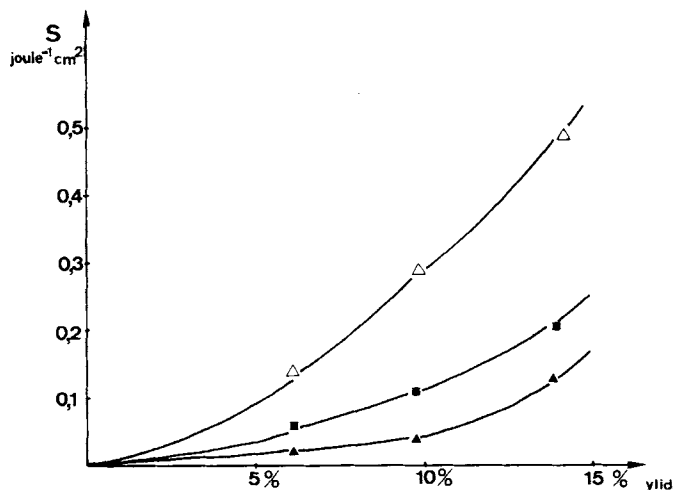
Fig. 6. Variation in sensibility with percentage of 4VP-ylid in 1-μ copolymers films: (▲) with UV filter; (■) without UV filter; (△) with 10% in bulk of sensitizer (Michler's ketone).

The variation of the sensibility versus percentage of 4VP-ylid in copolymers is shown in Figure 6. It shows the great influence of Michler's ketone on the crosslinking effect.

CONCLUSIONS

Polymeric materials containing pyridinium dicyanomethylide units can be easily synthetized from copolymers of 4-vinylpyridine and another suitable co-monomer. The λ_{max} of spectra is 410 nm. By irradiation with a mercury medium-pressure source they can be photoreticulated. The photosensitivity of these materials was determined using the so-called "photoresist test." The photosensitivity depends on the irradiation wavelength according to a curve as given in Figure 7. As a comparison, ylided copolymers are 50 times less sensible
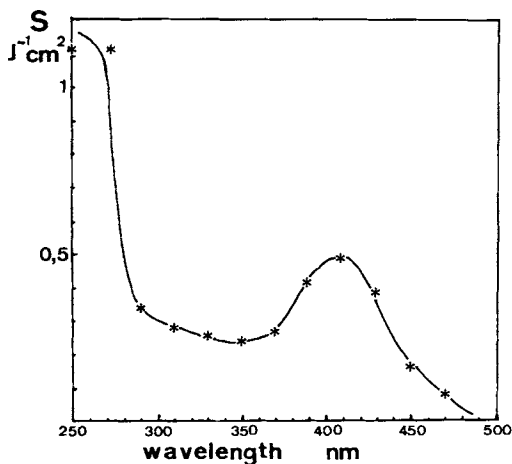
Fig. 7. Photosensitivity of a 1-μ film of sample 3 copolymer vs. wavelength (determined with monochromatic light $\Delta\lambda$ = 10 mm); I = 0.01 W/cm^2.

than commercial Kodak KPR. They are five times less sensible than poly(4-vinyl N-oxide).[3] An interesting advantage is that they can be irradiated through a glass plate.

The photoreticulation of polymer by cleavage of an ylid bond could be generalized to other ylid systems, inasmuch as the photocleavage of the ylid bond seems to be a general process.[4,19,13]

References

1. J. L. R. Williams, in *Polyelectrolytes*, E. Selegny, Ed., D. Reidel, Dordrecht, Holland, 1979, p. 507.

2. G. A. Delzenne, *Ind. Chim. Bèlge*, **39**, 249 (1974).

3. J. L. Decout, A. Lablache-Combier, and C. Loucheux, *Photogr. Sci. Eng.*, **23**, 309 (1979).

4. J. P. Catteau, P. Karafiloglou, A. Lablache-Combier, N. Lethan, and G. Surpateaun, *Tetrahedron*, **32**, 461 (1976).

5. S. M. Merril, C. C. Unruh, and E. M. Robertson, U.S. Pat. 2831768; *Chem. Abstr.*, **52**, 14400 (1958). C. David, W. Demerteau, and G. Geuskens, *Polym., G. B.*, **10**, 21 (1969).

6. W. J. Unn, O. W. Webster, and R. E. Benson, *J. Am. Chem. Soc.*, **87**, 16, 3651 (1965).

7. T. Tamikado, *J. Polym. Sci.*, **43**, 489 (1960).

8. M. Shtoo, *Photogr. Sci. Eng.*, **12**, 169 (1968).

9. A. Lablache-Combier, in *Photochemistry of Heterocyclic Compounds*, D. Burchard, Ed., Wiley–Interscience, New York, 1976, p. 207; F. Bellamy and J. Streith, *Heterocycles*, **4**, 1391 (1976).

10. Nastasi, H. Strub, and J. Streith, *Tetrahedron Lett.*, **51**, 4719 (1976).

11. W. Kirmuse, *Carbene Chemistry*, 2nd ed., Academic, New York and London, 1971.

12. Michler's ketone: triplet energy E_T = 61 kcal/mole, φ_{ic} = 1. Benzophenone: triplet energy E_T = 69 kcal/mole, φ_{ic} = 1. From *Handbook of Photochemistry*, S. L. Murov, Ed., Marcel Dekker, New York, 1973.

13. H. Arai, H. Igeta, and T. Tsuchiga, *Chem. Comm.*, 521 (1973).