

Photochemistry of Polymeric Systems. V.

Photocrosslinking of Polymers and Copolymers Containing Pyrazine Mono- and Di-*N*-Oxide Groups*

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Synopsis

Pyrazine mono- and di-*N*-oxide chromophores included in a polymeric chain induce its photoreticulation. Photosensitivity is higher for dioxidized samples than for monoxidized ones. The mechanism of photocrosslinking is different from the one which proceeds photoreticulation of polymeric chains containing pyridine *N*-oxide groups.

INTRODUCTION

In previous articles of this series¹ we reported that pyridine *N*-oxide² quino-*l*eine *N*-oxide, and pNN dimethylaminostyrene *N*-oxide³ included as a side chain of a polymeric material induce its photocrosslinking. The first step of this reaction is the photocleavage of the N—O bond, which is a triplet state reaction. The oxygen liberated by this cleavage abstracts a hydrogen, and the radicals so formed on different polymer chains combine, inducing crosslinking.

In this article we report the photocrosslinking of thin films of mono- or dioxidized pyrazine containing polymers or copolymers. We established that the photosensitivity is higher for dioxidized samples than for monoxidized ones. The mechanism of photocrosslinking appeared different from that previously reported for the photocleavage of *N*-monoazaaromatic oxidized groups.

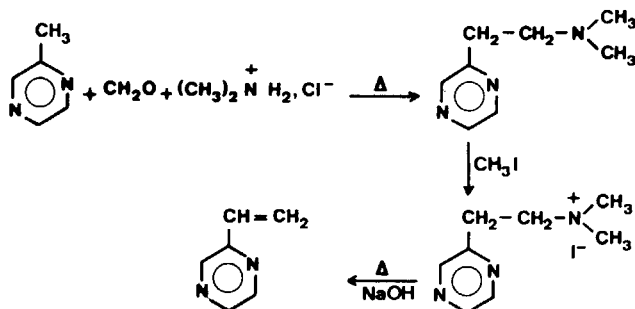
EXPERIMENTAL

Monomers

Vinylpyrazine (VPZ) is not a commercial monomer. It was synthesized from methylpyrazine (Aldrich) according to the process described by Kamal⁴ and shown as follows:

* Part IV is Ref. 1.

† Associated with l'Ens de Chimie de Lille, LA 351 of the CNRS.

Scheme 1. Synthesis of vinylpyrazine according to Kemal et al.⁴

The two first steps were a conventional Mannich reaction followed by a quaternization by CH_3I . The third step was a Hofmann degradation and with reference to methylpyrazine the cumulative yield was 12%. Vinylpyrazine was characterized by chromatography on silice plates (eluant: $\text{CHCl}_3/\text{CH}_3\text{OH}$, 80/20 v/v) and its $^1\text{H-NMR}$ spectrum.

Styrene (St) and methylmethacrylate (MMA) were Merck compounds. The monomers were distilled under vacuum just before use in order to remove polymerization inhibitor.

Polymerizations

Conventional radical polyaddition was performed at 60°C both for homo- and copolymerizations, α, α' -azoisobutyronitrile (AIBN) being used as the initiator. Pure monomer or both comonomers were dissolved in dioxane and degased by three thaw-pump cycles. The vessel was then sealed and held at 60°C during the time of polyaddition. Crude polymer or copolymers were recovered by precipitation in *n*-heptane. Final purification of the different materials was performed by dissolution in dioxane, precipitation in *n*-heptane and drying under vacuum at 40°C .

N-Oxidization of Polymeric Materials

Two oxidization techniques were used depending on the oxidization degree needed.

Room Temperature N-Oxidization. The oxidization reaction was performed in CHCl_3 solution during 3 h at 20°C in the presence of *m*-chloroperbenzoic acid. Acetone was then added to the medium in order to precipitate the oxidized samples. This method gives mainly mono-*N*-oxidized products.

High Temperature N-Oxidization. The reaction was carried out in acetic acid in the presence of hydrogen peroxide during 7 h at 75°C . Final purification was obtained by dissolution in formamide and precipitation in methanol. This method gives mainly di-*N*-oxidized products.

Characterization of Polymeric Materials

Nonoxidized Samples

Potentiometric Determinations. Due to the very low value of PK_B (0.6) of pyrazine ring, a potentiometric determination of the composition of different copolymers was impossible.

Spectrometric Determinations. Alkylpyrazine chromophore absorbs in the UV range. This allows a determination of the composition of copolymers with methyl methacrylate. The compositions found were compared with the results of quantitative analysis, taking into account the precision of the methods. The IR spectrometric characterization was made keeping in mind that pyrazine rings exhibit two strong bands at 1400 and 1020 cm^{-1} and two medium bands at 1145 and 1060 cm^{-1} .

Molecular Weights. All the values of number average molecular weights were determined in CHCl_3 by tonometric measurements (Knauer Vapor Pressure Osmometer) using benzyl as standard.

N-Oxidized Samples

UV Spectra. Taking methylpyrazine mono-*N*-oxide and methylpyrazine di-*N*-oxide as model molecules, an attribution of the peaks of *N*-oxidized polymeric samples could be made. In principle, the use of the corresponding values of the molar extinction coefficients must allow the quantitative determination of mono- and di-*N*-oxide groups both in homopolymers and copolymers.

Photoreticulation Studies

Photoreticulation of films of the different polymeric materials obtained was studied using the so-called "photoresist test."⁵ The irradiations were carried out with a medium pressure mercury source Philips SP 500. The time t needed to obtain the insolubilization threshold was determined, and the sensitivity of the material was deduced according to the relationship

$$S = K/It$$

where K is arbitrarily taken as 1 and I is the energy needed to produce insolubilization. The value of I was determined with a Kipp and Zonen Photopile. This photosensitivity depends on the emission spectrum of the radiation source used. If only a narrow range of wavelength is absorbed by the polymeric material, the value of S is minimized.

Spectrophotometric Studies of the Irradiated Films

The aim of this study was to determine UV and IR spectra of the polymeric films at different photocrosslinking ratios corresponding to different times of irradiation. The quantitative IR spectrometric studies were performed on films of constant thickness obtained by evaporation of a polymeric chloroform solution on a KBr pellet. The spectra were recorded using a Beckman IR 18 Spectrometer. The quantitative UV studies were carried out on films obtained by evaporation of a polymeric solution on quartz suprasil slides. An optical density of 1 for the maximum of absorption of the films was quite convenient for such studies. The spectra were recorded using a Perkin-Elmer UV-Visible 554 Spectrometer. For both IR and UV studies the irradiation source was the Philips SP 500 Medium-Pressure Mercury Lamp. Alternatively, a filter could be used to decrease the intensity of this light source.

TABLE I
 Copolymers St-VPz

Polymer no.	F_{St}	F_{VPz}	AIBN (mol/L)	Time (h)	τ	f_{VPz}	M_n
2	0.823	0.177	22×10^{-3}	56	2.6	0.39	3700
3	0.898	0.102	20×10^{-3}	56	2.9	0.22	7100
4	0.671	0.329	21×10^{-3}	64	2.9	0.55	4400

RESULTS AND DISCUSSION

Polymeric Samples

Nonoxidized Samples

The polymerization conditions of homopolyvinylpyrazine (P2VPz) were: monomer, 4 g in 4 mL of dioxane; initiator, AIBN 2.5×10^{-2} mol/L; polymerization temperature = 60°C; polymerization time = 64 h (31% conversion); M_n = 3500.

The typical conditions of copolymerization were: solvent dioxane (5 mL: 50% in weight); copolymerization temperature = 60°C; copolymerization time = 40 h.

Tables I and II give, respectively, the results and the conditions of copolymerization for St-VPz and MMA-VPz copolymers. In these tables F_i denotes the molar fraction of i repeat unit in the copolymer obtained, τ the conversion rate, and M_n the number average molecular weight.

In the IR spectrum of homopolyvinylpyrazine (P2VPz) the main bands are the same as for 2-methylpyrazine⁶ (3020 s, 1580 w, 1520 m, 1460 m, 1400 s, 1140 m; 1060 m, 1020 m, 840 m, 770-750 s). In the St-VPz copolymer there is an overlap between the bands of the pyrazinic group and of the benzenic one. The 1520 and 1400 cm^{-1} and 1020 cm^{-1} pyrazinic bands are separated.

In the MMA-VPz copolymer the bands of the two chromophores appear. The 1720 cm^{-1} (s) and 1200 cm^{-1} (s) band are characteristic of the ester function. In Table III are the UV data of P2VPz.

In the St-VPz copolymers there is a maximum at 266 nm and a shoulder at 257 nm due to the benzene ring. In NMA-VPz copolymers only the pyrazine ring absorbs in the 240-320 nm range.

Oxidized Samples

In the experimental conditions of *N*-oxidization of pyrazine rings, some oxidization of the main chain takes place simultaneously. Carboxylic and cetonic

 TABLE II
 Copolymers MMA-VPz

Polymer no.	F_{MMA}	F_{VPz}	AIBN (mol/L)	Time (h)	τ	f_{VPz}	M_n
5	0.813	0.187	21×10^{-3}	40	14	0.46	6600
6	0.896	0.104	34×10^{-3}	40	19	0.23	8000

TABLE III
UV Data of Homopolyvinylpyrazine

Solvent	λ	ϵ (L/mol-cm)
Chloroform	266	5350
	273	4400
	313	900
Water pH 7	266	5600

groups were detected by IR spectrometry. The polymeric samples were slightly yellow after oxidation.

In oxidized material both 1400 cm^{-1} and 1600 cm^{-1} bands of the pyrazinic ring decreased in intensity. A new band appeared at 1310 cm^{-1} in the mono-*N*-oxidized samples and at 1260 cm^{-1} for the di-*N*-oxidized ones.

UV data of mono- and di-*N*-oxidized homopolyvinylpyrazine are given in Table IV. (There are two 2-methylpyrazine *N*-oxides.) They have the same UV spectrum.⁸ In the homo- and copolymer mono-*N*-oxidized, the *N* which is oxidized cannot be determined. Moreover, the percentage of *N*-oxidization cannot be determined by elemental analysis due to the oxidation of the polymeric chain. The potentiometric method of Muth et al.⁷ allowed the determination of total oxidized nitrogen atoms excluding a precise evaluation of mono- and di-*N*-oxidized pyrazinic rings. The relative percentage of mono- and di-*N*-oxidization was determined from the molar extinction of UV spectra of the various homopolymers and copolymers synthesized, according to the theoretical ϵ values given in Table IV.

Table V gives the percent of mono- and di-*N*-oxidization for different samples: homopolyvinylpyrazine, oxidation in water at room temperature; copolymers 6' and 6'', oxidation in chloroform at room temperature and at 75°C in acetic acid.

The potentiometric method and the data taken from the UV spectra in the case of the other *N*-oxidized copolymers allow us to generalize these results. The oxidation in chloroform at room temperature leads to a copolymer in which roughly one pyrazinic ring over two is mono-*N*-oxidized, and the other one not oxidized (copolymer 3').

The oxidation in acetic acid at 75°C leads to a (co)polymer in which 70% of the pyrazinic ring is di-*N*-oxide, 15% is *N*-oxidized, and 15% is not oxidized (homopolymer 1', copolymers 2', 3', 4', 5'); accurate determination of the relative mono- and di-*N*-oxidization is difficult due to a chain oxidization.

TABLE IV
UV Data of Homopolyvinylpyrazine Mono- and Di-*N*-Oxide

In water	λ_{max} (nm)	ϵ^a (L/mol-cm)
Mono- <i>N</i> -oxide	217	15,100
	268	12,600
Di- <i>N</i> -oxide	227	12,100
	305	15,900

^a ϵ = theoretical values of the completely mono- or di-*N*-oxidized homopolymer. These values have been evaluated from the ϵ values of pyrazine Mono- and di-*N*-oxide.

TABLE V
Percentage of *N*-Oxidation of (Co) Polymers Containing Pyrazinic Ring vs. Oxidation Condition

No. polymer formed by oxidation	Starting polymer	Solvent	Temperature of oxidation	% of <i>N</i> -oxidation
1''	P2VPz 1	H ₂ O	Room	40% Mono- <i>N</i> -oxide 0% Di- <i>N</i> -oxide
6''	Copolymer MMA-VPz 77-23%	CHCl ₃	Room	48% Mono- <i>N</i> -oxide 0% Di- <i>N</i> -oxide
6'		CH ₃ COOH	75°C	70% Di- <i>N</i> -oxide 16% Mono- <i>N</i> -oxide

Study of Photoreticulation

Table VI gives the photosensitivity of the (co)polymers synthesized. It is measured without any filter. A large amount of the light emitted by the mercury medium-pressure source is not absorbed by the different (co)polymers.

The nonoxidized homopolymer P2VPz (polymer 1) is slightly photosensitive. The pyrazinic ring photoexcited abstracts hydrogen in the chain.⁹ The radicals so formed, combined, induce the reticulation. The pyridinyl ring induces also the photoreticulation of homopolyvinylpyridine but in this case the photosensitivity is 10 times² smaller than in the one of P2VPz (29×10^{-3} vs. 3×10^{-3} cm²/J).

Oxidation of the pyrazinic ring induces a strong increase of the photosensitivity of the polymer. Di-*N*-oxidized (co)polymers are more photosensitive than mono-*N*-oxidized ones.

The photosensitivity of a polymer must increase with its molecular weight. It is clearly the case in the systems studied.

TABLE VI
Photosensitivity of the Different Polymers Prepared

Polymer no.	Polymer	Molecular weight \bar{M}_n before oxidation	Solvent	S cm ² /J
	Commercial KPR Kodak + sensitizer products		Ethylene glycol acetate	10
	P.E. 4125 (Kodak) + sensitizer		Butylphthalate	25
1	P2VPz	3450	Formamide	0.029
1'	P2VPz di- <i>N</i> -oxide		Formamide	0.84
1''	P2VPz mono- <i>N</i> -oxide		Formamide	0.506
2'	Co St-VPz (61-39) ^a di-NO	3700	Formamide	1.32
3'	Co St-VPz (78-22)di-NO	7100	Chloroform	1.5
3''	Co St-VPz (78-22)mono-NO		Chloroform	0.463
4'	Co St-VPz (46-54)di-NO	4400	Formamide	1.4
5'	Co MMA-VPz (54-46)di-NO	6000	Formamide	0.95
6'	Co MMA-VPz (77-23)di-NO	8000	Chloroform	0.55
	4VPNO	165,000	Methanol + water (5%)	1.2

^a Composition of the polymers are given in %.

The photosensitivity of the di-*N*-oxidized homopolymer 1' ($\overline{M}_n = 3450$) is smaller than the one of copolymer 3' ($\overline{M}_n = 7100$). However, the percentage of photosensitive groups is much higher for 1' than for 3'.

For comparable molecular weight and percentage of photoreactive groups, styrene copolymers are slightly more photosensitive than methyl methacrylate ones; it was the opposite for similar copolymers with vinylpyridine *N*-oxide.² The photosensitivity of the poly(vinyl-4 pyridine) *N*-oxide (P4VPNO) homopolymer we studied before² is slightly higher than the one of mono- or di-*N*-oxidized homopolyvinylpyrazine 1'' and 1' (1.2 vs. 0.502, 0.84). The molecular weight of the P4VPNO polymer being 50 times higher than the one of 1'' or 1', it can be concluded that the photosensitivity induced by a mono- or di-*N*-oxidized pyrazinic ring is higher than the one induced by a pyridinic *N*-oxide group.

Figure 1 gives the variation of the photosensitivity of a 1- μ m-thick film of sample 3' (co St-2VPz 78-22%) as a function of the wavelength. The photosensitivity varies as the absorption spectrum.

UV Spectrophotometric Studies

Di-N-Oxidized Homopolyvinylpyrazine (Polymer 1')

Figure 2a shows that when a film of P2VPz di-NO is irradiated, the 315 nm absorption band (it corresponds to a π - π^* transition of the pyrazine di-*N*-oxide chromophore) decreases rapidly. The 268 nm band (corresponding to a π - π^* transition of the pyrazine mono-*N*-oxide chromophore) varies simultaneously. A detailed study of this part of the UV spectrum [Fig. 2(b) shows that there is an increase of absorption in the 268 nm range with two isobestic points at 284 and 248 nm during the first 30 s of irradiation]. For a longer irradiation time, the absorption by the film decreases, but it remains a maximum of absorption at 268 nm.

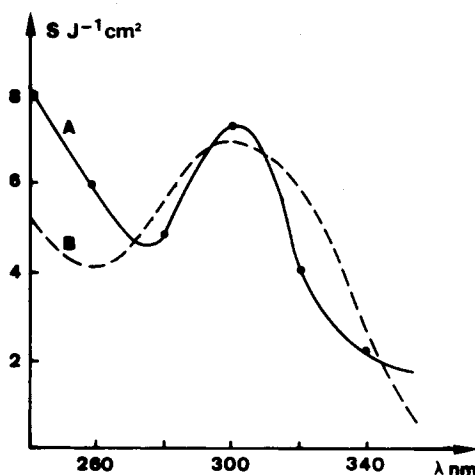


Fig. 1. Photosensitivity (A) and UV absorption (in CHCl_3) (B) of a 1- μ m film of Co St-2VPz (78-22%) di-NO (3') vs. wavelength (determined with a monochromatic light of $\Delta\lambda = 20$ nm).

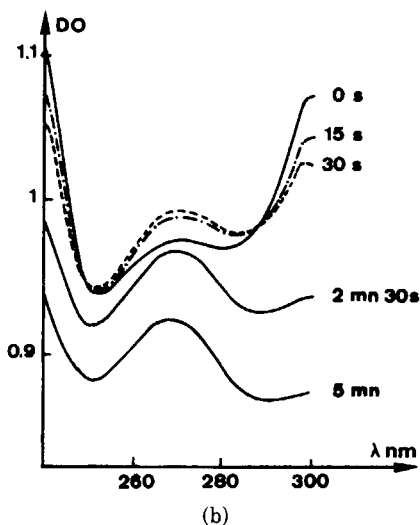
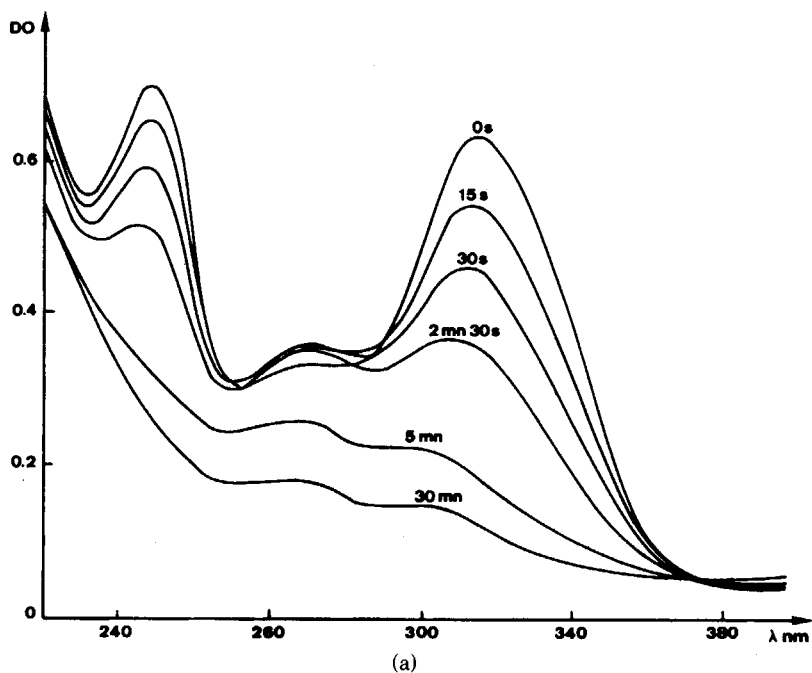


Fig. 2. Variation of UV spectrum of a 1- μm film of homopolyvinylpyrazine di-*N*-oxide as a function of irradiation time (irradiation source: a Philips SP 500 Medium-Pressure Hg Lamp) ($I = 3 \times 10^5$ erg/cm²-s in the 250–800-nm range): (a) evolution of the total UV spectrum; (b) evolution of the UV spectrum in the 240–300 nm range.

Mono-N-Oxidized Copolymer Styrene-Vinylpyrazine (78–22%)
(Polymer 3^o)

Figure 3 shows a decrease of the 268 nm peak (it corresponds to a π - π^* transition of the pyrazinic mono-*N*-oxide ring) in the first minute of irradiation. An

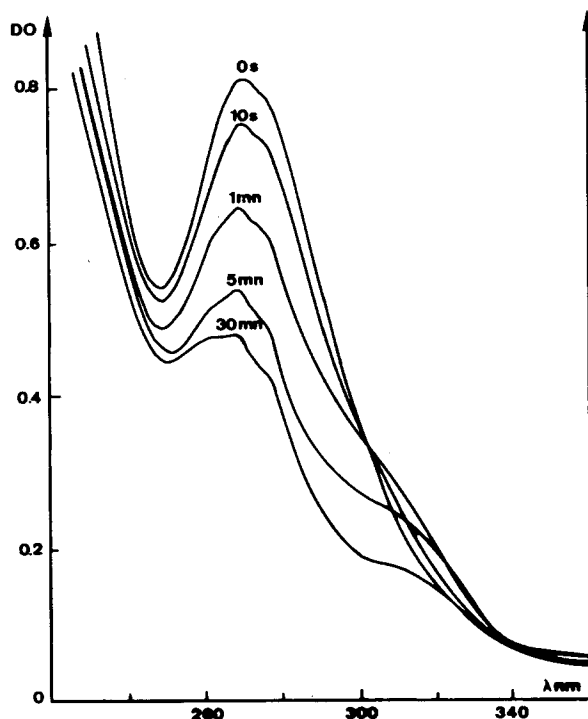


Fig. 3. Variation of the UV spectrum of 1- μm film of copolymer styrene-vinylpyrazine [78-22% mono-*N*-oxidized (polymer 3')] as a function of irradiation time (irradiation source: a Philips SP 500 Medium-Pressure Hg Lamp) ($I = 3 \times 10^5$ ergs/cm²-s in the 250-800 nm range).

isobestic point at 300 nm appears. After 30 min the spectrum does not change any more. It has a maximum at 268 nm and a shoulder at 310 nm.

Reaction Ratio

If we define a reaction ratio τ by the equation

$$\tau = \frac{(D\lambda_t - D\lambda_0)}{(D\lambda_0 - D\lambda_\infty)} \times 100$$

where $D\lambda_t$ is the optical density of a film at the wavelength of its λ_{max} at time t , $D\lambda_0$ the optical density of the film at the wavelength of its λ_{max} at time $t = 0$, $D\lambda_\infty$ the optical density at the film at the wavelength of its λ_{max} corresponding to the residual absorption after a long period of irradiation.

We can see in Figure 4 that, for a short period of irradiation, the mono-*N*-oxidized pyrazinic chromophore is more reactive than the di-*N*-oxidized one: it disappears more rapidly during the first 30 s of irradiation.

IR Spectrophotometric Studies

Di-N-Oxidized Copolymers

Di-*N*-Oxidized Styrene-2 Vinylpyrazine Copolymer (78-22%) (Polymer 3'). It can be deduced from Figure 5 that the 1260 cm⁻¹ band characteristic of

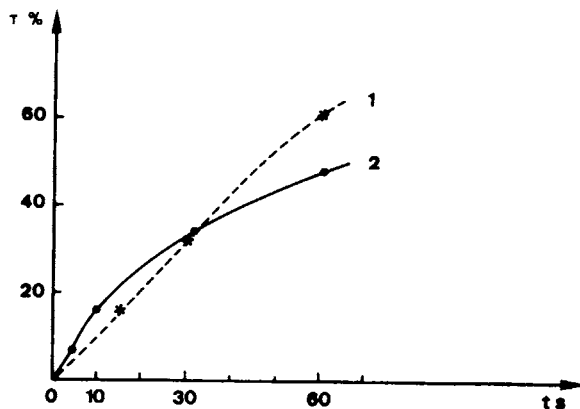


Fig. 4. Reaction ratio vs. irradiation time measured for 1- μ m film: (1) polymer 1': homopoly-vinylpyrazine di-*N*-oxidized; (2) polymer 3'': copolymer styrene-vinylpyrazine (78-22%) mono-*N*-oxidized.

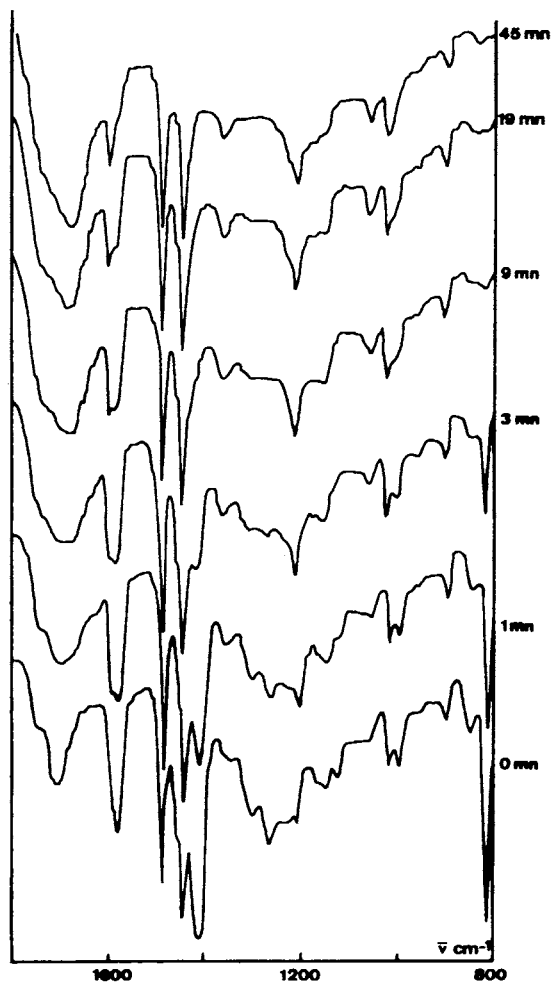


Fig. 5. Variation of the IR spectrum of Co St-2VPz (78-22%) di-*N*-oxidized (polymer 3'') when irradiated with a polychromatic light ($I = 0.14 \text{ W/cm}^2$ in the range 220-800 nm).

the pyrazine di-*N*-oxide chromophore decreases rapidly when the film is irradiated. The intensity of the 1310 cm^{-1} band characteristic of the mono-*N*-oxide groups does not increase in the meantime. Simultaneously the bands characteristic of the pyrazinic aromatic ring ($1590, 1400, 1150, 1010, 820\text{ cm}^{-1}$) decrease.

Di *N*-Oxidized Copolymer Methyl Methacrylate-2 Vinylpyrazine (77-23%) (Polymer 6'). A similar phenomenon is observed (Fig. 6). There is a decrease of the $1260, 1400,$ and 820 cm^{-1} bands. It can be seen in Figures 5 and 6 that the bands characteristic of the pyrazinic ring do not appear when the films are irradiated. The bands characteristic of the alkylbenzene or of the methyl methacrylate remain after irradiation.

Mono-N-Oxidized Copolymers

When a film of a mono-*N*-oxidized copolymer is irradiated, the 1310 cm^{-1} band characteristic of the *N*-oxidation decreases. The IR spectrum of the polymer

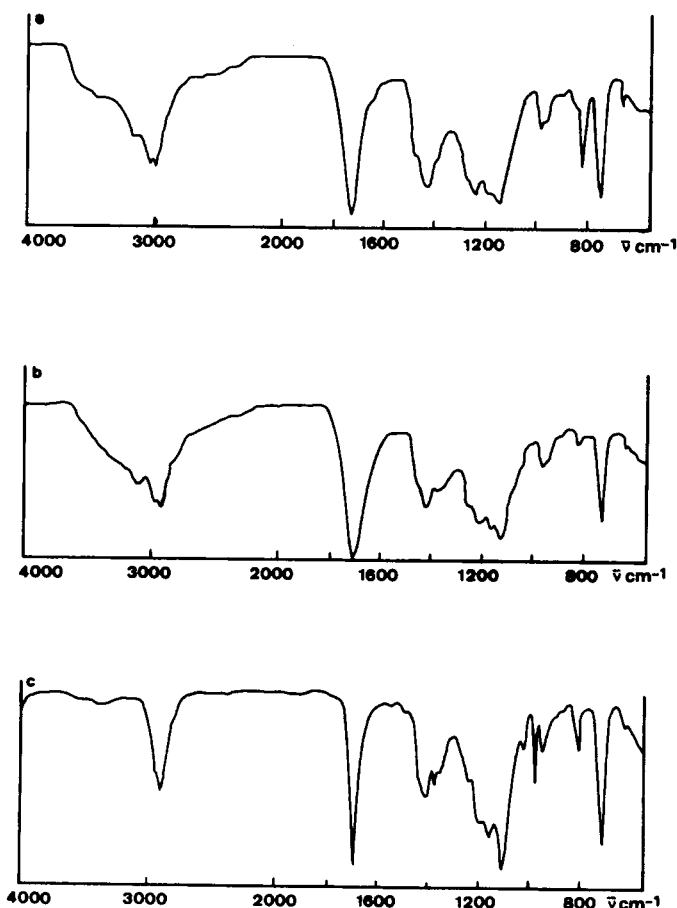


Fig. 6. Variation of IR spectrum of Co MMA-2VPz (77-23%) di-*N*-oxidized (polymer 6') when irradiated with a polychromatic light ($I = 0.14\text{ W/cm}^2$ in the range 220-800 nm): (a) $t = 0\text{ min}$; (b) $t = 30\text{ min}$; (c) IR spectrum of co MMA-2VPz (77-23%) (polymer 6).

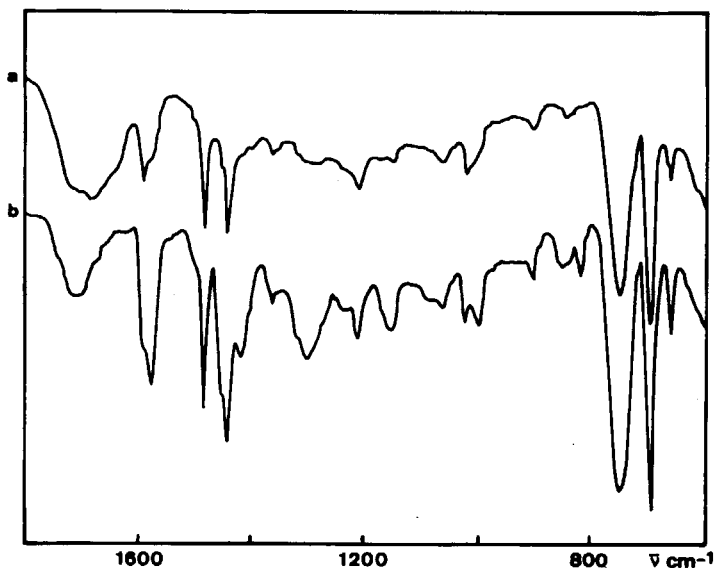


Fig. 7. Variation of the IR spectrum of a Co St-2VPz (78-22%) mono-*N*-oxidized (polymer 3') when irradiated by a polychromatic light ($I = 0.14 \text{ W/cm}^2$ in the 220-800 nm range): (a) $t = 19 \text{ min}$; (b) $t = 0 \text{ min}$.

obtained after a long irradiation is different from the one of the corresponding nonoxidized copolymer (see Fig. 7).

Mechanism of the Photoreticulation

When polyvinylpyridine *N*-oxide homopolymer or copolymers of vinylpyridine *N*-oxide are irradiated in similar conditions, the polymer is transformed in the corresponding pyridinic homo- or copolymer.² The *N*-oxide bond cleavage is a triplet state reaction. The oxygen liberated in this photoreaction abstracts a hydrogen on the polymeric chain. $\text{NO}\cdot$ and polymeric radicals are so formed. Their recombination induces the reticulation.² UV and IR data in the case of di-*N*-oxide pyrazinic polymers and IR data in the case of the mono-*N*-oxide one show clearly that after irradiation the oxidized polymer is not converted into the nonoxidized one. To be sure that such reaction does not occur very rapidly and is followed by a reaction of the nonoxidized polymer, we compared the IR spectrum of di-*N*-oxidized copolymer 3' [St-2VPz (78-22%)] irradiated for 45 min and the IR spectrum of copolymer 3 [St-2VPz (78-22%)] irradiated in the same conditions during the same time. They are clearly different (cf. Fig. 8). In fact, the IR spectrum of copolymer 3 is nearly the same before UV irradiation and after 45 min of UV irradiation.

From these data it can be concluded that pyrazinic mono- or di-*N*-oxide chromophores do not induce the photoreticulation of a polymer by the same mechanism as pyridine *N*-oxide² quinoline *N*-oxide or dimethylaminostyrene *N*-oxide chromophore do.³ It can be seen from the IR spectrum of di-*N*-oxidized copolymer 3' [St-2VPz (78-22%)] that during its synthesis from copolymer 3

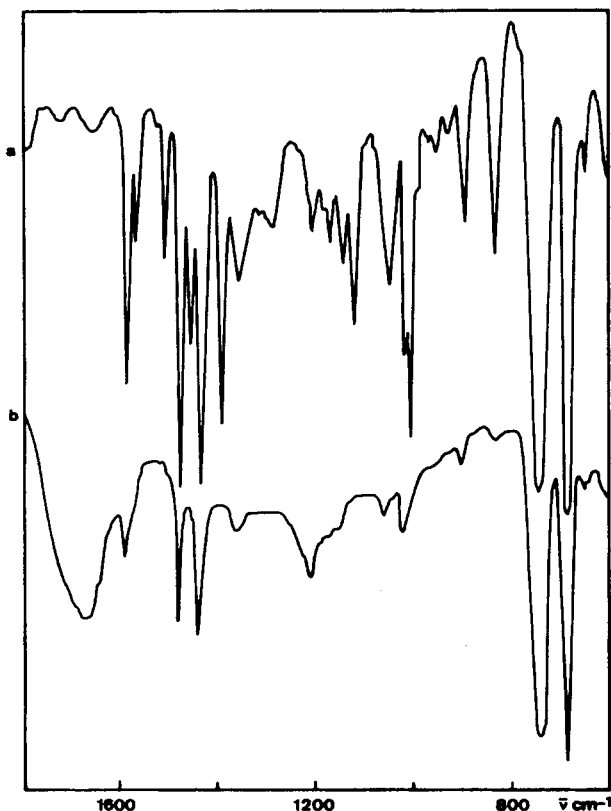
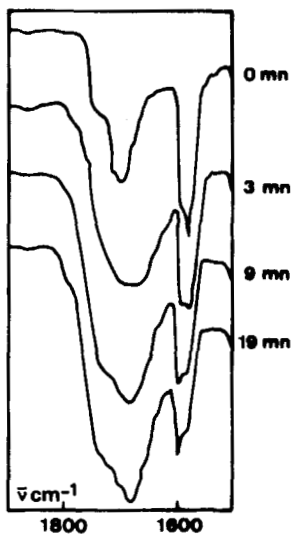


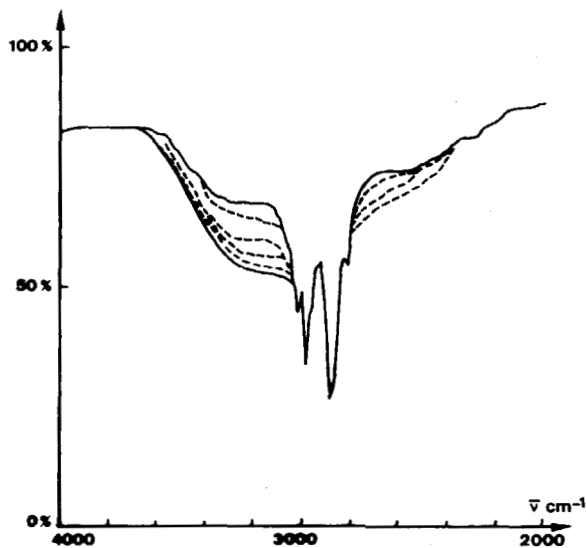
Fig. 8. Comparison of the IR spectra of a film of: (a) Co St-2VPz (78-22%) (polymer 3) and (b) Co St-2VPz (78-22%) di-*N*-oxidized (polymer 3') after 45 min of irradiation with a Philips SP 500 Medium-Pressure Hg Lamp.

[St-2VPz (78-22%)] the main chain is oxidized. The formation of ketones on the chain occurs simultaneously with the *N*-oxidization of the pyrazinic rings [cf. Fig. 9(a)]. During UV irradiation of this di-*N*-oxidized copolymer 3', a large amount of carbonyl chromophores are produced. Similarly the amount of the —OH groups on this copolymer increases [cf. Fig. 9(b)]. When a copolymer of 4-vinylpyridine *N*-oxide is irradiated on the same conditions, carbonyl and hydroxyl bonds are also formed, but in a much smaller amount.²

In copolymer 3', 70% of the pyrazinic rings are di-*N*-oxidized, 15% monooxidized. The formation of a great quantity of carbonyl and, above all, of hydroxyl groups during UV irradiation of this copolymer is consistent with the photo-reaction of the corresponding small molecules: pyrazine di-*N*-oxide in aqueous solution is converted in dihydroxypyrazines¹⁰ whereas 2,5-dimethylpyrazine-1 mono-*N*-oxide is converted in 2-acetyl-2,5-methylimidazole and in 2,5-dimethylimidazole when irradiated in benzene, but in a hydroxypyrazine and in an open chain olefin substituted by 2-amido groups when irradiated in water¹¹ (see Scheme 2). It is worth noticing that pyrazine mono-*N*-oxide does not seem to be a primary product of pyrazine di-*N*-oxide and that no pyrazine is formed from either of these compounds.^{10,11}



(a)



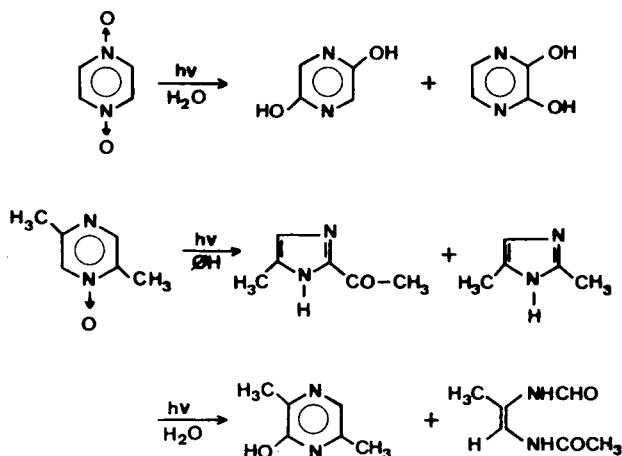
(b)

Fig. 9. Variation of the IR spectrum of a 10- μm film of Co St-2VPz (78-22%) di-*N*-oxidized (polymer 3') irradiated by a polychromatic light ($I = 0.14 \text{ W/cm}^2$ in the 220-800 nm range): (a) in the 1800-1600 cm^{-1} part of the spectrum; (b) in the 2200-3600 cm^{-1} part of the spectrum; (1) $t = 0, 3$ min; (3) $t = 9, 19$ min; (5) $t = 30, 45$ min.

The change of the electronic spectrum of pyrazine di-*N*-oxide during UV light illumination in aqueous neutral solution is very similar to the one we reported for homo-2-vinylpyrazine di-*N*-oxide (polymer 1').¹⁰

Quenching of the Photoreticulation

The cleavage of the N—O bond of monoazaaromatic *N*-oxide is a triplet reaction. The photosensitivity of (co)polymers in which the reactive group is



Scheme 2. Photoreactivities of pyrazine di-*N*-oxide and of 2,5-dimethylpyrazine *N*-1-oxide.^{10,11}

pyridine *N*-oxide,² quinoline *N*-oxide or poly-*N,N*-dimethylaminostyrene *N*-oxide is enhanced by triplet photosensitizers.

We studied the influence of such photosensitizers on di-*N*-oxide copolymers St-2VPz (78–22%) (polymer 3') 10% in weight of the photosensitizer is added to a solution of this copolymer, before the formation of the 1- μm film. Xanthone (ET = 74.2 kcal/mol) has no effect on the photosensitivity of polymer 3', whereas benzophenone (ET = 69.8 kcal/mol) decreases (by 20%) its photosensitivity. (The photosensitivity is measured in these two experiments with the same procedure as before, using all the light emitted by a Philips SP 500 Medium-Pressure Mercury Lamp.)

When rubrene (ET = 25 kcal/mol), which is a good triplet quencher, is added to polymer 3', the photosensitivity of this polymer decreases by 40%. In this experiment a light of $\lambda = 260$ nm with $\Delta\lambda = 20$ nm is used to measure the photosensitivity. Rubrene absorbs 10% of this incident light.

We can conclude from the experiments that a triplet state of the polymer 3' is involved in the photoreticulation process. Its energy is in the same order as that of xanthone. It is quenched by benzophenone. This does not prove that a singlet state is not also a reaction state.

CONCLUSION

It can be concluded from the data we reported here that both pyrazine mono-*N*-oxide and pyrazine di-*N*-oxide groups borne by the side chain of a polymer can induce its photoreticulation. The reticulation efficiency of the di-*N*-oxide chromophore is higher than the one of the mono-*N*-oxide. The efficiency of both of them is higher than that of pyridine *N*-oxide, quinoline *N*-oxide or polydimethylaminostyrene *N*-oxide. The mechanism inducing the photoreticulation by irradiation of mono- and di-*N*-oxide pyrazinic chromophore is not the same as for azaaromatic amine mono-*N*-oxides. In the case of pyrazine derivatives the photochemical reaction does not involve a break of the N—O bond, as it does in the case of monoazaaromatic derivatives.

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