Macromolecules **1982,** *15,* 435-438

< 1 would be observed. For a beautiful example of this type of behavior in poly(vinylcarbazole) films, see ref 1a.

(11) (a) The ionization potentials are as follows: naphthalene, 8.12 eV; pyrene, 7.58 eV (Matsen, F. A. *J. Chem. Phys.* **1956,** *24,* 602). (b) The quenching constant of Py fluorescence by TCNB is quite large (4600 M^{-1}) as measured by: Grellmann, K. H.; Watkins, A. R.; Weller, A. *J. Phys. Chem.* **1972,** *76,* 3132.

(12) If $^3Py^*$ is populated by triplet excitons with a lifetime on the order of that of isolated $^3Py^*$, the effect will be apparent lengthening of $\tau_{^3Py^*}$.

(13) Kim, N., unpublished results.

(14) According to Möhwald and Sackmann (Möhwald, H.; Sackmann, E. *Z. Naturforsch., A* **1974,** *29A,* 1216) the triplet state of Py–TCNB pairs in a 1:1 naphthalene–TCNB CT crystal is lower by 1400–2200 cm^{-1} than the naphthalene–TCNB triplet exciton. This energy gap is similar to what we observed for the P2VN phosphorescence (λ_{max} ~540 nm) and the structureless emission with λ_{max} ~610 nm.

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Photolysis of Cyclooctyl Nitrite in Solution and in Polymer Medium

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ABSTRACT: The photolysis of cyclooctyl nitrite in solution and in polymeric medium has been followed spectrophotometrically (ultraviolet and infrared). In solution the quantum yield of photolysis, Φ_N, varies between 0.5 and 0.6, depending on the solvent, while in polymer films, it is only about 0.25 on account of enhanced radical cage recombination. On the contrary, the quantum yield of cyclooctanone formation, Φ_K, is much higher in film (0.16 in poly(vinyl chloride)) than in solution (0.08 in dichloromethane); the cyclooctanone results from the disproportionation reaction between the NO radical and the cyclooctyloxy radical within the photolytic cage. Moreover, on the basis of the absence of a nitroso derivative in polymeric medium, it must be concluded that no Barton reaction takes place in film and that cyclooctanone becomes the main reaction product of photolysis.

The Barton reaction is based on the photolysis of alkyl nitrites to alkoxy radicals, followed by intramolecular hydrogen abstraction by the latter and recombination of the resulting carbon radicals with nitrogen oxide to form nitroso derivatives or oximes.[1] The structural requirement of this reaction is that the alkoxy radicals should be formed in potentially close proximity of a hydrogen atom from the δ-carbon atom through a six-membered cyclic transition state.[2-4] In the case of cyclooctyl nitrite, 4-nitroso-1-cyclooctanol dimer is formed by transannular attack of the oxy radical without a noticeable ring-cleavage mechanism.[5] The alkoxy radical produced by photolysis must be axial for intramolecular abstraction of the δ-hydrogen atom. This abstraction includes therefore a conformational change of the cyclooctane ring, while the most stable conformation presents the nitrite in equatorial position.[6] The Barton reaction thus requires in this case a conformational ring mobility, which makes cyclooctyl nitrite well suited for studying the influence of the reaction medium and particularly of a polymeric matrix on the course of this rearrangement. Conversely, it could afford further information about chain segment mobility in polymeric systems.[7,8] It is that aspect that will be considered in the present paper.

Experimental Section

Ultraviolet and infrared spectra were recorded on Perkin-Elmer 124 and 580B spectrophotometers, respectively. NMR spectra were taken on a Varian Associates XL spectrometer. Glass transition temperatures were determined with a Perkin-Elmer Model 2C differential scanning calorimeter (DSC).

Tetrahydrofuran was used in forming the polymer films of PVC and P(VDC-*co*-VC). The other polymers were cast from dichloromethane.

The light intensity values were determined with an IL700 research radiometer fluxmeter (International Light) with a PT1710 no. 1005 detector.

Cyclooctyl nitrite was prepared by reaction of cyclooctanol with nitrosyl chloride.[9] In dichloromethane solution it presents a characteristic nitrite absorption band with λ_{max} 374 nm ($\epsilon_{CH_2Cl_2}$ = 60 L mol^{-1} cm^{-1}). The other, more intense absorption varies with the solvent; e.g., in methylene chloride and in hexane, λ_{max} is equal to 247 nm ($\epsilon_{CH_2Cl_2}$ = 1330 L mol^{-1} cm^{-1}) and 240 nm ($\epsilon_{C_6H_{14}}$ = 1540 L mol^{-1} cm^{-1}), respectively. Most solvents and polymeric matrices interfere, however, with the absorption measurements of this band.

Table I
Quantum Yield of Photolysis of Cyclooctyl Nitrite in Solution[a]

solvent[b]	Φ_N	solvent[c]	Φ_N
dichloromethane	0.56 (0.54)	isopropyl acetate	0.45 (0.44)
diethyl ether	0.67	methanol	0.69 (0.60)
acetonitrile	0.57	ethanol	0.42
cyclohexane	0.50		
n-hexane	0.49		
trichlorotrifluoroethane	0.55		

[a] Values in parentheses correspond to photolysis under an inert atmosphere. [b] Solvents with isosbestic points. [c] Solvents without isosbestic points.

Irradiations were carried out under nitrogen at room temperature using an Osram HB200 high-pressure mercury lamp with an interference filter (λ 367 nm). The photolyses were followed spectrophotometrically in different solvents on the basis of the absorption at 374 nm. The optical densities varied from 0.5 to 1.6 in dichloromethane (30 mg of nitrite in 10 mL of solvent); ketone formation with time was followed by measuring the carbonyl infrared absorption at 1690 cm^{-1}. In trichlorotrifluoroethane the nitroso dimer precipitates during irradiation;[5] it was redissolved in methanol and refluxed for 2 days to form the corresponding 4-oximino-1-cyclooctanol. The oily reaction product was analyzed by IR and NMR. The yield of oxime was determined gravimetrically and by NMR. Polymer films were prepared by casting solutions of 5 wt % polymer and 1 wt % nitrite on a mercury surface. After evaporation of the solvent under an inert atmosphere, the films were dried under vacuum at room temperature. After irradiation the polymer was examined and analyzed by infrared spectrometry (carbonyl absorption) and by UV

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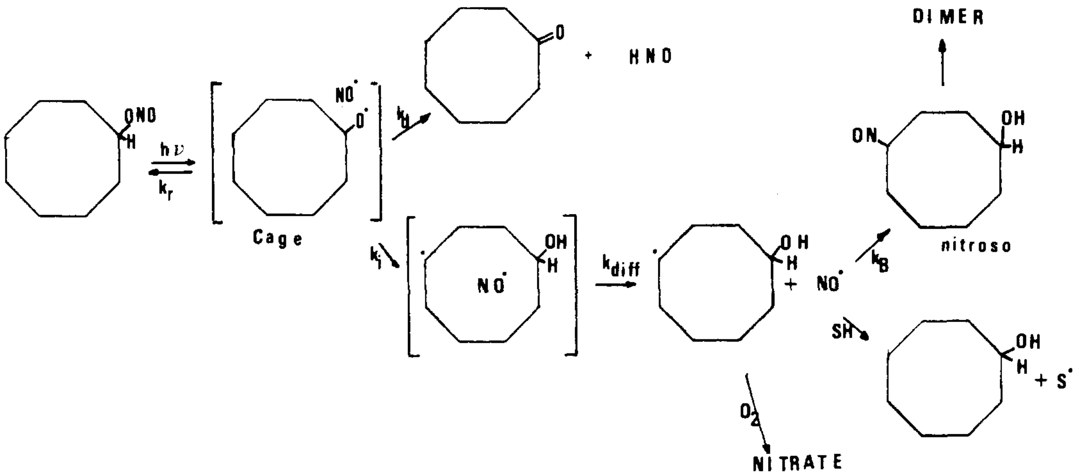
Scheme I



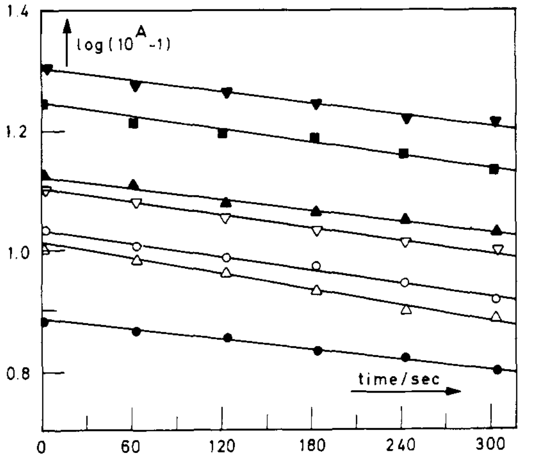


Figure 1. Determination of quantum yields of cyclooctyl nitrite photolysis in solution (λ_{irr} 367 nm): (▼) *n*-hexane; (▲) cyclohexane; (▽) acetonitrile; (○) trichlorotrifluoroethane ($CFCl_2$-CF_2Cl); (●) ethanol; (■) dichloromethane; (△) diethyl ether.

spectrometry (nitrite absorption).

Photolysis in Solution

The photolysis of cyclooctyl nitrite in different solvents was followed spectrophotometrically. By plotting the optical density at λ_{max} against the time, one can easily determine the quantum yields of photolysis, Φ_N, from the slopes, equal to $\epsilon_{max} I_0 \Phi_N$,[10] knowing ϵ_{max} (60 L mol^{-1} cm^{-1}) and the incident light intensity (Figure 1). The quantum yields in different solvents are given in Table I; their values differ slightly but are not influenced by the presence of atmospheric oxygen.

In most solvents the ultraviolet absorption spectra during irradiation show a well-defined isosbestic point at 340 nm, which results from the formation of a nitroso dimer (λ_{max} 290 nm, $\epsilon_{CH_2Cl_2}$ = 6000 L mol^{-1} cm^{-1}). However, in methanol and ethanol, no intersection of absorption curves is observed; H abstraction from the solvent produces indeed cyclooctanol and prevents formation of a nitroso derivative. Isopropyl acetate behaves as an intermediate case (Figure 2).

The quantum yield of ketone formation, Φ_K, i.e., the number of ketone molecules formed per absorbed photon, was also determined on the basis of the increasing carbonyl infrared absorption band (1690 cm^{-1}, ϵ = 452 L mol^{-1} cm^{-1}). In dichloromethane solution it is 0.08 (0.07 under nitrogen). The efficiency of ketone formation, E_K, i.e., the number of moles of ketone per decomposed nitrite, is thus Φ_K/Φ_N = 0.13. It is not affected by the presence of oxygen.

Under an inert atmosphere a nitroso dimer is formed. Its yield in trichlorotrifluoroethane, in which the dimer precipitates,[5] amounts to about 80%. As expected no dimer is formed in the presence of oxygen.

From these results it can be concluded that the Barton reaction is the main process in the photolysis of cyclooctyl

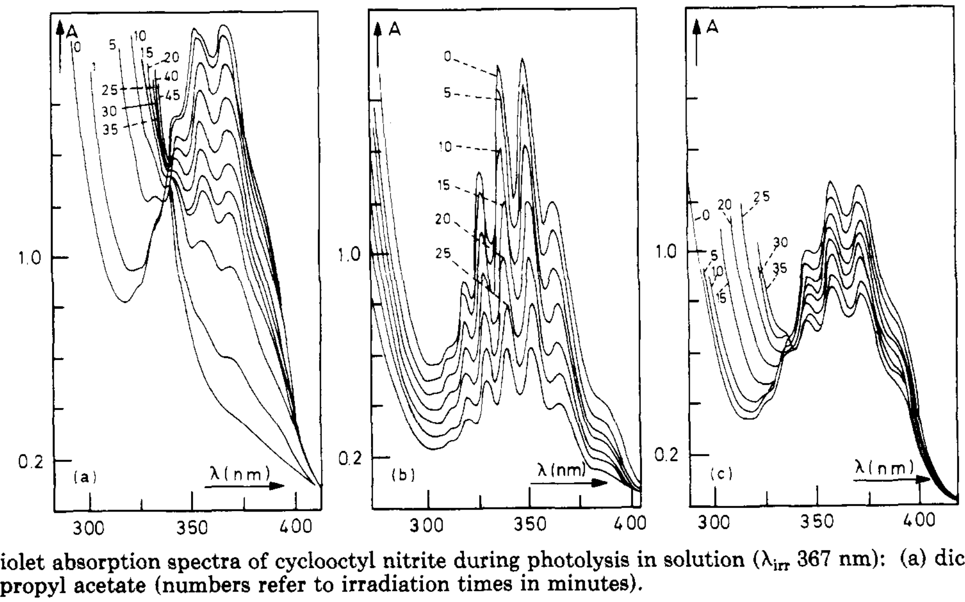


Figure 2. Ultraviolet absorption spectra of cyclooctyl nitrite during photolysis in solution (λ_{irr} 367 nm): (a) dichloromethane; (b) methanol; (c) isopropyl acetate (numbers refer to irradiation times in minutes).

Table II
Quantum Yield of Photolysis of Cyclooctyl Nitrite in Film[a]

polymeric matrix	symbol	T_g (exptl),[b] °C	Φ_N
poly(vinyl acetate)	PVAc	+1	0.10
poly(methyl methacrylate)	PMMA	+51	0.20 (0.15)
poly(vinylidene chloride-75-*co*-vinyl chloride-25)	P(VDC-*co*-VC)	−7	0.26
poly(vinyl chloride)	PVC	+15	0.28[c] (0.25)
poly(vinyl chloride) + 20% diglyme		+5	0.22

[a] Values in parentheses correspond to photolysis under an inert atmosphere. [b] T_g determined by differential scanning calorimetry of films containing around 20% cyclooctyl nitrite. [c] Φ_N = 0.26 at 3 °C.

nitrite in solution, which can be represented by the reactions in Scheme I.[3,11,12] Within the cage of radicals after photolysis, cage recombination of the radicals (k_r) and ketone formation (k_d) compete with intramolecular hydrogen transfer (k_i), which is required for the subsequent steps of the Barton reaction (k_B). As should be expected, atmospheric oxygen is without noticeable effect on the different cage processes and does not affect Φ_N and Φ_K. On the contrary, nitroso compound formation and its dimerization occur only after diffusion out of the cage and are strongly affected by the presence of oxygen and/or hydrogen-donating solvents.

Photolysis in Polymer Films

Cyclooctyl nitrite was photolyzed at room temperature in different polymer matrices in order to evaluate the influence of the nature of polymer and its glass transition temperature. The quantum yields of photolysis, Φ_N, are given in Table II.

From comparison of Tables I and II, the following conclusions can be drawn:

1. In polymer matrices Φ_N is much lower (less than half) than in solutions on account of an enhanced radical recombination in the photolytic cage (k_r) due to a strong decrease of diffusion possibilities.
2. Φ_N varies slightly between 0.2 and 0.28 and is thus almost insensitive to the nature of the matrix. In poly(vinyl acetate) cyclooctyl nitrite decomposes in the dark with discoloration of the film, likely due to oxidation of the matrix.
3. Φ_N is insensitive to oxygen and to the glass transition temperature of the matrix.

During irradiation the ultraviolet absorption spectra present no isosbestic points (Figure 3); the strong decrease of absorption at 290 nm indicates the absence of nitroso dimer formation. Nitroso monomer, which should be characterized by an absorption at 680 nm, also was not detected. NMR analysis of the reaction products shows clearly the presence of ketone formation but the absence of nitroso compounds and oxime.

Ketone formation was followed quantitatively in poly(vinyl chloride) film (T_g = 15 °C) on the basis of the increasing infrared ketone absorption at 1690 cm^{-1} (Figure 4). The values of the corresponding quantum yields (Φ_K) and ketone formation efficiencies (E_K) are given in Table III and compared with those in dichloromethane. Though Φ_N in film is less than half that in solution, the ketone formation efficiency, E_K, is 4–5 times larger in polymer film, so that the ketone becomes the main reaction product

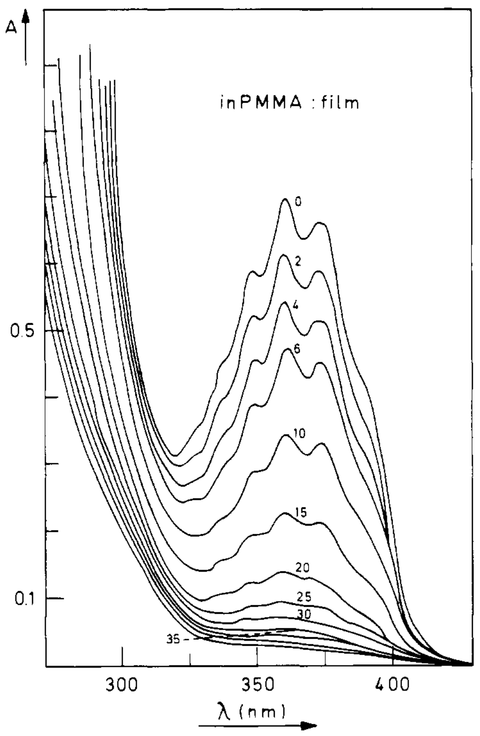


Figure 3. Ultraviolet absorption spectra of cyclooctyl nitrite during photolysis in poly(methyl methacrylate) film (λ_{irr} 367 nm) (numbers refer to irradiation times in minutes).

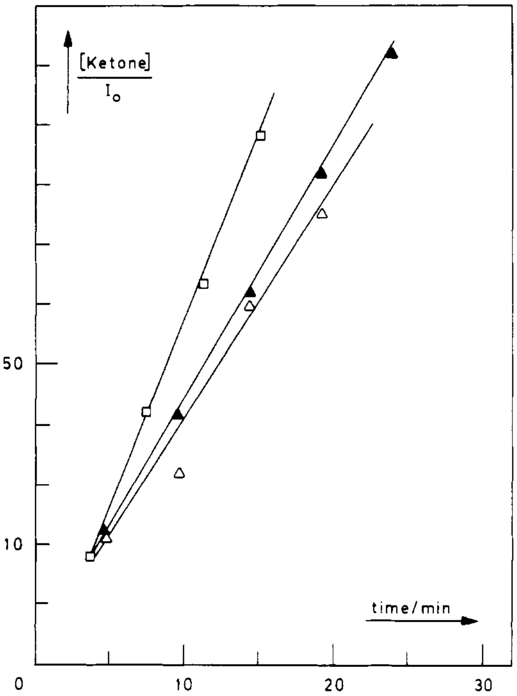


Figure 4. Determination of quantum yield of cyclooctanone; formation in poly(vinyl chloride) film (λ_{irr} 367 nm): (□) room temperature, air; (▲) room temperature, nitrogen; (△) 3 °C, air.

Table III
Quantum Yield of Ketone Formation, Φ_K, and Ketone Formation Efficiencies, E_K

reaction medium	Φ_N	Φ_K	E_K	remarks
dichloromethane	0.6	0.08	0.13	room temp, air
dichloromethane	0.54	0.07	0.13	room temp, under N_2
poly(vinyl chloride)	0.28	0.15	0.54	room temp, air
poly(vinyl chloride)	0.25	0.17	0.68	room temp, under N_2
poly(vinyl chloride)	0.26	0.18	0.69	3 °C, air

of photolysis. On the basis of these data it must be concluded that practically no Barton reaction takes place in the polymeric matrix. The ketone formation results from hydrogen abstraction of the alkoxy radical by the NO radical (k_d) followed by disproportionation within the cage with simultaneous formation of hyponitrous acid.

The intramolecular H transfer (k_i), which requires a boat–chair conformation of the cyclooctane ring, necessitates a conformational ring mobility that is strongly reduced in the polymeric matrix. The two main reactions for the cage radicals are thus recombination (k_r) to cyclooctyl nitrite, which is responsible for the much lower quantum yield of photolysis in film than in solution, and disproportionation (k_d) to cyclooctanone and hyponitrous acid, which accounts for the high ketone formation efficiency E_K. In polymeric medium, formation of a nitroso monomer and/or oxime is therefore strongly reduced and is estimated at a maximum of 10%. Absence of a nitroso dimer results evidently from lack of diffusion in the solid medium. It is noteworthy that the physical state of the matrix (below and above T_g) does not affect the quantum yields Φ_N and Φ_K.

Conclusion

The photolysis of cyclooctyl nitrite in polymeric medium differs considerably from that in solution. Limited interconversion of ring conformations is responsible for a lower quantum yield of photolysis and for formation of cyclooctanone as the main reaction product in polymeric medium, instead of nitroso compound as expected from the Barton reaction.

Acknowledgment. We are indebted to the Ministry of Science and Scientific Programmation for supporting this research and to IWONL, Belgium, for a fellowship (C.J.).

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Kinetics of Polycondensation and Copolycondensation by Amide-Interchange Reactions

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Received August 12, 1980

ABSTRACT: Low molecular weight amino-terminated polyamides were synthesized via amide-interchange reactions of diamine amides of dibasic acids. The kinetics of polycondensation and copolycondensation by amide-interchange reactions were investigated by using *N,N′*-bis(2-aminoethyl)sebacamide and *N,N,N′,N′*-bis(diethylenimino)sebacamide as monomers. It was found that the polycondensation followed second-order kinetics with respect to the concentrations of amino and amide groups in the monomers at the initial stage of the reaction. The rate constants of cross reactions in the copolycondensation and the diamine component ratios incorporated into the copolymer were determined from the equations derived. The reactivity ratios of the copolycondensation were calculated on the basis of the rate constants.

Introduction

Syntheses of polyamides can be categorized into three groups:[1] (1) heating the dibasic carboxylate salts of diamines, (2) reacting diamines with dibasic acid esters, and (3) reacting diamines with dibasic acid chlorides. In addition, amino-terminated polyamides can be obtained by polycondensation of diamine amides of dibasic acids by amide-interchange reactions in a manner analogous to the synthesis of hydroxy-terminated polyesters by polycondensation of diol esters of dibasic acids by ester-interchange reactions.[2]

Low molecular weight amino-terminated polyamides are expected to be potential prepolymers in the syntheses of high polymers since they are difunctional and the amino groups have high reactivity. The amino-terminated polyamides, in fact, can be easily incorporated into polyurethane elastomers. The succeeding polyamide blocks modify the physical properties of the polyurethane significantly.

In this paper we report syntheses of amino-terminated polyamides and the kinetics of polycondensation and copolycondensation of diamine amides of dibasic acids by amide-interchange reactions.

Kinetics

Polycondensation. The polycondensation of the diamine amides of dibasic acids by amide-interchange reactions can be expressed in general terms as

$$n\mathrm{H_2NRNHOCR'CONHRNH_2} \rightarrow \mathrm{H(HNRNHOCR'CO)}_n\mathrm{NHRNH_2} + (n-1)\mathrm{H_2NRNH_2} \qquad (1)$$

When the diamines formed during the polycondensation are removed, polyamide is left behind.

0024-9297/82/2215-0438$01.25/0