increase to −0.36 and −0.42 kcal mol^{-1}, respectively.

An increase in temperature causes a decrease in the $g^{\pm}g^{\pm}$ conformations about two consecutive C–C skeletal bonds and, consequently, the dipole moments of the chains increase. Values of the temperature coefficient as a function of E_α and E_β are given in the fourth column of Table III. It can be seen that in increasing E_α and E_β from −0.42 and −0.66, respectively, to −0.36 and −0.42, the value of 10^3d ln $\langle\mu^2\rangle/\mathrm{d}T$ decreases from 2.3 to 1.4.

The best agreement between the calculated values of both the dipole moment ratio and its temperature coefficient with the experimental ones ($\langle\mu^2\rangle/nm^2 = 0.35$ and 10^3d ln $\langle\mu^2\rangle/\mathrm{d}T = 4.5$ at 30 °C) is obtained for the values of E_α and E_β given in the first row of Table III. The relatively low values of these conformational energies suggest that in this polymer, as in the other members of the polyoxetane series, particular effects stabilizing gauche conformations about C–C skeletal bonds are important.

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Registry No. 2-Methyloxetane, 2167-39-7; poly(2-methyloxetane) (homopolymer), 26100-60-7.

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Ring-Opening Reactions of a Bicyclic Aziridine in Polymeric Medium

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ABSTRACT: Upon irradiation above 290 nm, bicyclic aziridines give an ylide intermediate whose stability depends on the structure of the aziridine. The photolysis of 2,2-dimethyl-4-phenyl-6-(*p*-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene (DNBH) has been studied in solution and in a polymer matrix. In solution the quantum yield of enediimine formation, Φ_I, increases with temperature ($\Phi_I \cong 0.3$ at 35 °C). In poly(methyl methacrylate), $\Phi_I = 0.75$ above its T_g, while $\Phi_I = 0.3$ below T_g. Ylide fading, i.e., ylide cyclization into bicyclic aziridine and/or ylide isomerization into enediimine, is about 10 times slower in polymeric medium as compared to the solution and does not obey first-order kinetics. Consequently, the behavior in polymeric medium differs considerably from that in solution with respect to the rate of reaction and the relative importance of enediimine formation.

It has been shown by Trozzolo and co-workers[1] that the photolysis of bicyclic aziridines involves a C–C bond scission with the formation of a colored azomethine ylide intermediate[2]

In this respect the bicyclic aziridine 2,2-dimethyl-4-phenyl-6-(*p*-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene (DNBH) is particularly attractive.[3] On irradiation above 290 nm in the crystalline state and in the glassy state, it develops a transient blue color due to ylide formation; this color change is reversible. On the basis of trapping experiments with dimethyl acetylenedicarboxylate and tetracyanoethylene as dipolarophiles, Trozzolo showed[4] that the ylide resulting from the photolytic disrotative ring cleavage first isomerizes into the syn-4-ylide, which may then give a cycloadduct and either return back to the initial compound or isomerize into enediimine. Moreover, the formation of two isomeric ylides was easily shown by the presence of two absorption maxima in the visible spectrum after photolysis at low temperature.[5] This enediimine formation is similar to that described by Padwa and Glazer[6] in the case of the 2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene.

The scheme shown in Figure 1 summarizes this photolytic and thermal behavior of DNBH.[7] Although a thermal

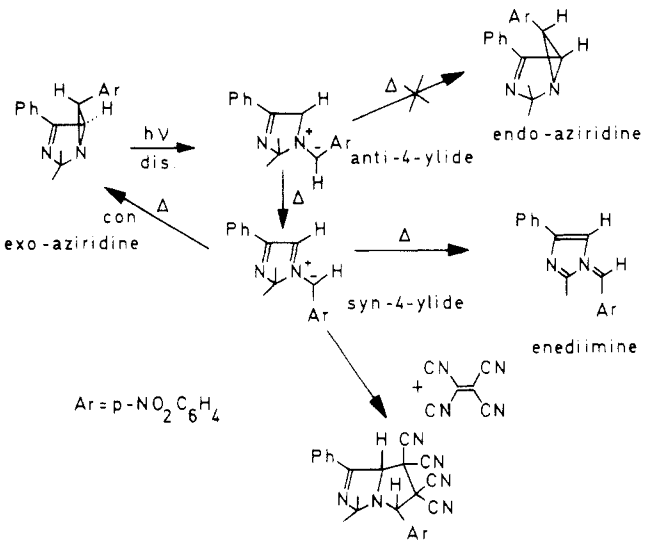

Figure 1. Photolysis of bicyclic arizidine DNBH.

cyclization of the anti-4-ylide into the endo aziridine is conceivable, this reaction has never been detected, probably because of the important steric hindrance it would involve. It should also be mentioned that the homologue seven-membered bicyclic aziridine 5-phenyl-7-(*p*-nitrophenyl)-1,4-diazabicyclo[4.1.0]hept-4-ene[8] behaves similarly to DNBH.

Considering the steric limitations imposed by such processes, it seems interesting to examine the effect of a solid reaction medium, i.e., a polymeric matrix, on these ring opening/ring closure and isomerization reactions. In this sense, a double comparison between reactions in solution and polymer film will be described, one related to the formation of enediimine and the other to the thermal decoloration of the intermediate ylide.

Experimental Section

DNBH was synthesized by condensation of 2-benzyl-3-(*p*-nitrophenyl)aziridine with acetone and alcohol in the presence of a large amount of ammonia.[9] Reaction kinetics were followed spectrophotometrically. DNBH has two strong absorption bands in the UV spectrum with λ_{max} at 250 nm (ϵ = 14 000 L·mol^{-1}) and 289 nm (ϵ = 12 050 L·mol^{-1}).

Irradiations were carried out at room temperature (except when indicated) with an Osram HB200 high-pressure mercury lamp with a monochromator at 300 nm. On irradiation in dichloromethane solution ($\sim 10^{-4}$ M), the optical density decreases, and the formation of enediimine can be followed at 400 nm as a function of time (ϵ = 10 700 L·mol^{-1}) (Figure 2). The enediimine absorbs, however, in the region of irradiation; this inner-filter effect has to be taken into account in determining the light intensity absorbed by DNBH using the following equation:

$$I_{abs}^{DNBH} = I_0 \frac{OD_{DNBH}}{OD_{tot}}(1 - 10^{-OD_{tot}})$$

in which OD_{DNBH} is the optical density due to DNBH absorption and OD_{tot} represents the total optical density.

Observation of intermediate ylide (λ_{max} = 580 nm) requires a high irradiation intensity and use of a band filter from 300 to 400 nm instead of a monochromator. The ylide decoloration is a fast reaction that proceeds thermally; it can be followed spectrometrically in the visible spectrum at 580 nm in solution and in film.

Polymer films were cast from dichloromethane solutions. Their glass transition temperatures were determined with a Perkin-Elmer Model 2C differential scanning calorimeter (DSC).

Experimental Results

Enediimine Formation. The quantum yield of enediimine formation, Φ_I (Table I), can easily be determined from variations of the optical density at 400 nm against I_{abs} × time of irradiation, the slope of the diagram being equal to $10^3\epsilon\Phi_I I_0$. Irradiations were carried out in dichloromethane at 15, 25, and 35 °C. Φ_I increases with increasing temperature and was equal to 0.17, 0.28, and 0.33, respectively.

Table I
Photolysis of DNBH in Polymeric Matrices[a]

polymer	T_g, °C	temp of irrad, °C	Φ_I[b]
poly(methyl methacrylate)	50	15	0.3
		25	0.3
		35	0.28
		50	0.75
		63	0.78
poly(vinylbutyral)	27	20	0.27
poly(vinyl acetate)	27	15	0.26
		20	0.28
		50	0.48

[a] 0.8-1 mg of DNHB/g of polymer. [b] Quantum yield of enediimine formation.

Table II
First-Order Reaction Rate Constant of Fading

t, °C	$10^2 k_1$, s^{-1}
15	4.6
19	5.4
26	11.4
38	23

When the irradiations are carried out in polymer matrices, e.g., in PMMA films, the spectral changes are similar to those observed in solutions (Figure 2). Noteworthy is, however, the peculiar temperature dependence of Φ_I. Below the glass transition temperature T_g, Φ_I is almost constant, equal to 0.27–0.30 (at 20 °C) and independent of the nature of the polymer. Above T_g, values as high as 0.75 are obtained; they exceed considerably those in solution.

It is assumed that above T_g, the ylide can achieve a planar structure and consequently isomerizes easily in enediimine; the ring closure requires, however, a transfer of the bulky $ArNO_2$ group into a plane vertical to that of the ylide. Such rotation is much more difficult in a high-viscosity polymer matrix than in solution, and consequently the relative importance of the competitive ring closure is diminished.

In the glassy state ($<T_g$), the ylide cannot reach easily the planar structure and sticks almost in its original position. It can therefore easily return to the bicyclic aziridine, and ring closure becomes as important as in solution.

Ylide Cyclization. After intense irradiation of a 10^{-3} M solution of DNBH in dichloromethane a transient blue color with an absorption band at 580 nm due to the intermediate ylide is formed; its decoloration can easily be followed as a function of time. The fading is very fast, at least in solutions, and proceeds through a first-order reaction mechanism (Table II).

Similarly, a polymer film (8 mg/g of polymer) colors immediately on irradiation and shows an absorption maximum at 580 nm. Its thermal decoloration is, however, about 10 times slower than in solutions and shows a strong deviation from first-order reaction kinetics (Figure 3), as has been often observed for reactions in polymer.[10] It is admitted that the ylides are present in different strained physical conditions resulting from a nonequilibrium distribution of the free volume in the film after casting. Moreover, light absorption may cause local heat effects, which also should influence the ring closure.

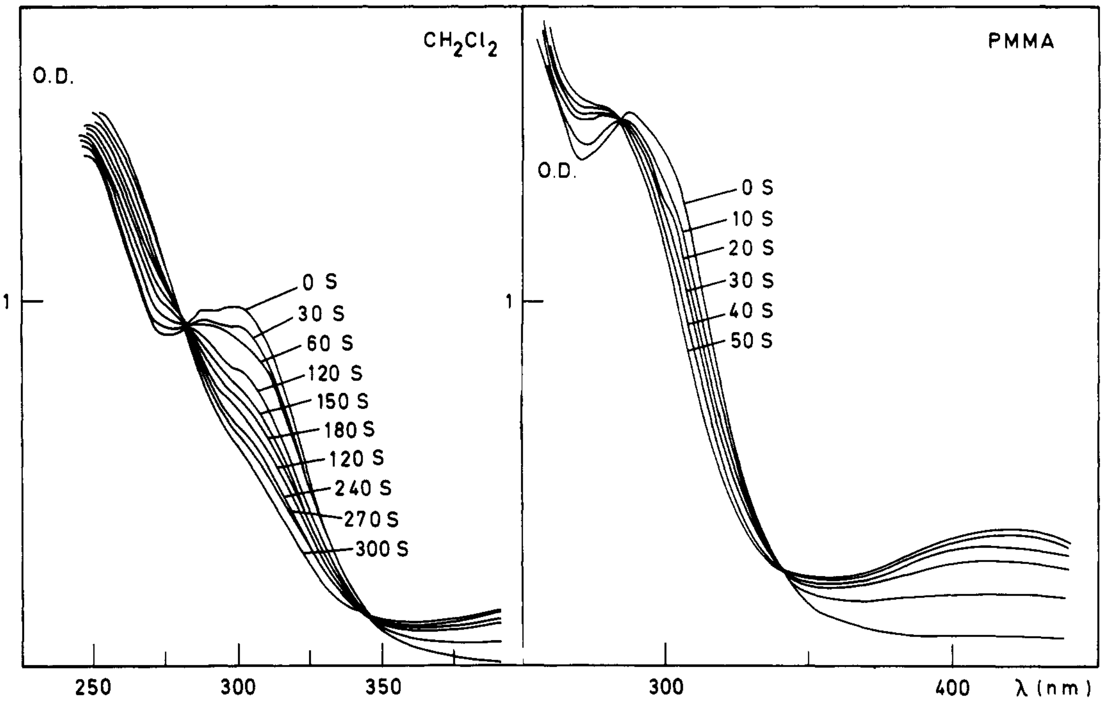

Figure 2. Changes of ultraviolet spectra of diazabicyclohexene (DNBH) with time of irradiation (in seconds) (λ_{irr} = 350 nm): left, in dichloromethane solution (10^{-4} M); right, in PMMA film.

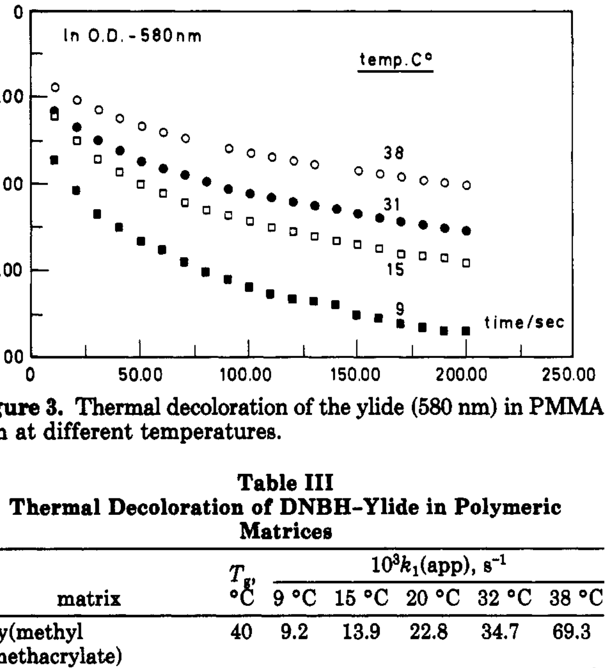

Figure 3. Thermal decoloration of the ylide (580 nm) in PMMA film at different temperatures.

Table III
Thermal Decoloration of DNBH-Ylide in Polymeric Matrices

matrix	T_g, °C	10^3k_1(app), s^{-1} 9 °C	15 °C	20 °C	32 °C	38 °C
poly(methyl methacrylate)	40	9.2	13.9	22.8	34.7	69.3
poly(vinylbutyral)	16	1.9	4.6	6.9[a]	17.3	19.8[b]
poly(vinyl acetate)	5		3.6	7.7[c]	11.5[d]	34.6[e]

[a] At 24 °C. [b] At 37 °C. [c] At 19 °C. [d] At 27 °C. [e] At 40 °C.

By determination of half-times of decoloration of the ylide, "apparent" rate constants of fading have been evaluated in three different matrices at different temperatures. The results are summarized in Table III. In poly(vinylbutyral) and poly(vinyl acetate) the rate of fading is markedly lower than in poly(methyl methacrylate), though the rates were measured above the glass transition temperatures.

Conclusion

The influence of a polymeric medium on the photochromic behavior of diazabicyclohexene (DNBH) is very pronounced. When the photolysis is carried out above T_g, the quantum yield of enediimine formation exceeds considerably that obtained in solution. The polymer matrix influences also the rates of thermal fading of the intermediate ylide. The rates are much lower than in solution and do not obey first-order kinetics.

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Registry No. Poly(methyl methacrylate) (homopolymer), 9011-14-7; poly(vinyl acetate) (homopolymer), 9003-20-7; DNBH, 13591-65-6.

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