ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 110 (1997) 23–28

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A: CHEMISTRY

Reversible cis–trans photoisomerization of poly(methacryloyloxyethyl-3-*N*-*n*-butylaminocrotonate) pendant group

I. Lukáč [a,*], Cs. Kósa [a], U. Salz [b], N. Moszner [b]

[a] *Polymer Institute, Slovak Academy of Sciences, SK 842 36 Bratislava, Slovak Republic*
[b] *Ivoclar AG, Bendererstrasse 2, FL-9494 Schaan, Liechtenstein*

Received 16 April 1997; accepted 19 May 1997

Abstract

The photochemical transformation of poly-(methacryloyloxyethyl-3-*N*-*n*-butylaminocrotonate) (PMAC), and its low-molecular-weight model compound ethyl-3-*N*-*n*-butylaminocrotonate (AC), was studied using 313 nm monochromatic light. The changes in the IR and UV spectra of the irradiated PMAC film and AC solution correspond to cis–trans isomerization. The reverse dark trans–cis isomerization of PMAC and AC is also observed, and the rate constants of the processes are determined. © 1997 Elsevier Science S.A.

Keywords: Photoisomerization; Poly(methacryloyloxyethyl-3-*N*-*n*-butylaminocrotonate)

1. Introduction

The investigation of the properties of enamines is of considerable interest because the enamino group is present in many complicated natural compounds [1]. The low-molecular-weight enamines are used in organic synthesis to prepare heterocyclic compounds and alkaloids which are of importance in medicine [2]. Polymeric enamines, as biodegradable materials, have been used as carriers of biologically active compounds [3].

The photo-oxidation of low-molecular-weight enamino ketones, enamino esters and enamino amides has been applied to synthesize 1,2-diketones, 2-ketoesters and 2-ketoamides [4]. Singlet oxygen takes part in this process. The reaction can also proceed in an "autosensitized" manner.

In previous work, the photochemical transformations of poly-(methacryloyloxyethyl-3-*N*-*n*-butylaminocrotonate) (PMAC) and ethyl-3-*N*-*n*-butylaminocrotonate (AC) were studied on irradiation with polychromatic ($\lambda > 300$ nm) light in the presence of oxygen [5]. The photoreaction resulted in irreversible changes, with different reaction paths observed in the solid film and in solution.

This study deals with the primary photochemical reactions of PMAC in a polymeric film and the low-molecular-weight model AC in solution on irradiation with low-intensity monochromatic light at $\lambda = 313$ nm.

2. Experimental details

2.1. Chemicals

PMAC and AC were prepared according to Refs. [5,6]. $M_w = 37\,800$ and $M_n = 10\,700$ of PMAC were estimated by size exclusion chromatography using polystyrene calibration. PMAC became insoluble after storing in the dark in air at room temperature. For example, a completely crosslinked film of PMAC was obtained under these conditions after 36 days. Crosslinking was not accompanied by changes in the IR spectrum. Therefore, to prevent crosslinking, PMAC was stored in $CHCl_3$ solution under an inert atmosphere in the dark at −20 °C. The solvents used were of analytical purity.

2.2. Equipment

The IR spectra were measured on Specord IR M80 (Zeiss, Jena, Germany) and FTIR Nicolet 400 (Nicolet, Germany) spectrometers. UV spectra were measured on a Specord M40 spectrometer (Zeiss, Jena, Germany). Proton nuclear magnetic resonance (^1H NMR) spectra were measured on a Bruker 300 spectrometer.

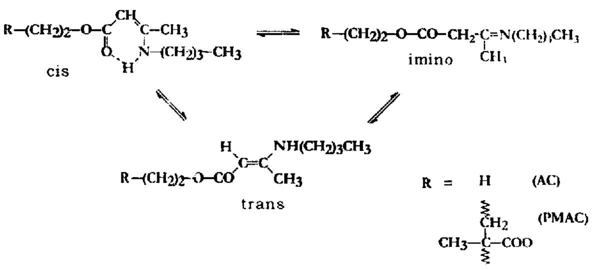
2.3. Irradiation

For irradiation at $\lambda = 313$ nm at 25 °C, a merry-go-round equipped with a medium-pressure mercury arc without a glass

---

[*] Corresponding author.

PII S1010-6030(97)00165-2



Scheme 1.

bulb (125 W, Tesla Holesovice, Prague, Czech Republic), placed in a cylindrical three-walled quartz reactor, was used. The cooling water circulated in the inner space of the reactor. A combination of chromate [7] and Corning glass filters was used to isolate the monochromatic light at 313 nm. The chromate filter was placed in the outer space of the reactor. A Corning glass filter N 7-59 (9863) (thickness, 0.5 cm) was situated in front of the sample in a metallic rotating holder. The distance of the sample from the centre of the lamp was 12 cm.

The PMAC films were cast from $CHCl_3$ (0.5 ml) solution containing 0.14 mg of PMAC onto quartz glass (2.5 cm × 4 cm) or by applying 0.8 ml of $CHCl_3$ solution containing 4 or 16 mg of PMAC on a KBr plate (2 cm × 4 cm). To secure a constant position during the measurements, the glass and KBr plates were fixed in the holder.

The AC solutions were irradiated in quartz cells ($d = 1$ mm) for UV measurements ($c = 0.0674$ g l^{-1}) and in KBr cells ($d = 0.61$ mm) for IR measurements ($c = 5.5$ g l^{-1}).

3. Results and discussion

3.1. Characterization of aminocrotonate group

The cis and trans isomers of *N*-substituted 3-enaminoesters can generally exist in equilibrium with each other, and also with the tautomeric imine form (Scheme 1) [8]. The stability of the isomers depends on the substituent on the nitrogen atom and on the polarity of the solvent [8]. For AC, the cis enamino ester form has been reported [8] to be thermodynamically most stable. In addition to published data, an equilibrium between the cis enamino ester (96%) and the tautomeric imino form (4%) has been found in this work by ^1H NMR measurements in $CDCl_3$. The concentration of the tautomers can be calculated from the integrals of the chemical shifts of $-NH-\underline{CH_2}-$ ($\delta = 3.25$ ppm, enamino form) and $=N-\underline{CH_2}-$ ($\delta = 3.00$ ppm, imino form) and also $\underline{CH_3}-C=CH-$ ($\delta = 1.90$ ppm, enamino form) and $\underline{CH_3}-C=N-$ ($\delta = 2.25$ ppm, imino form). The proportions of the cis enamino and tautomeric imino forms remain unchanged after storage of the solution for 10 days in the dark at 4–8 °C.

When an AC solution is prepared in wet (δ for H_2O, 4.80 ppm) deuteromethanol (CD_3OD), ^1H NMR reveals an increase in the imino form concentration from 10% (measured immediately after the preparation of the solution) to 23.5% (after storing the solution in the dark at 4–8 °C for 10 days) (Fig. 1). At the same time, a decrease in the signals of hydrogen-bonded $-N\underline{H}-$ at $\delta = 8.5$ ppm, $-C\underline{H}=C-$ at $\delta = 4.4$ ppm and $-\underline{CH_2}-COO-$ is observed due to equilibration and replacement by deuterium.

In addition to the ^1H NMR spectrum of AC, the above changes in the tautomeric forms can be followed by UV and IR measurements in methanol solution. Since the imino groups formed absorb in the wavelength region 170–200 nm [9], i.e. the region which cannot be used for measurements in methanol solution, the decrease in absorption at 285 nm has been selected to follow the enamino–imino tautomerization. Similar to ^1H NMR, the UV measurements reveal the same conversion of the enamino to imino form after the storage of AC in methanol solution in the dark for 10 days. In addition, the IR spectrum shows, qualitatively, an increase in the absorption of the imine group at 1635 cm^{-1} during the storage of AC in methanol solution in the dark.

The influence of the increased polarity of the solvent (wet methanol) is manifested by a shift in equilibrium from the cis to the imino form and not to trans.

3.2. Irradiation of AC in solution

To understand the photochemistry of PMAC more clearly, the photochemistry of AC was studied in different solvents. Significant differences in the $\pi-\pi^*$ absorption band of the UV spectrum are observed on irradiation of hexane and methanol solutions of AC. On irradiation of AC in hexane solution, a decrease in absorption at 285 nm and the formation of a new absorption band with a maximum at 267 nm are observed (Fig. 2). Similarly, the intensity of absorption at 285 nm decreases and a new absorption band with a maximum at 278 nm is formed on irradiation in methanol solution (Fig. 3). The new absorption band of AC in methanol solution is more intense than that in hexane solution. The isosbestic points in the UV spectra of AC irradiated in hexane and methanol

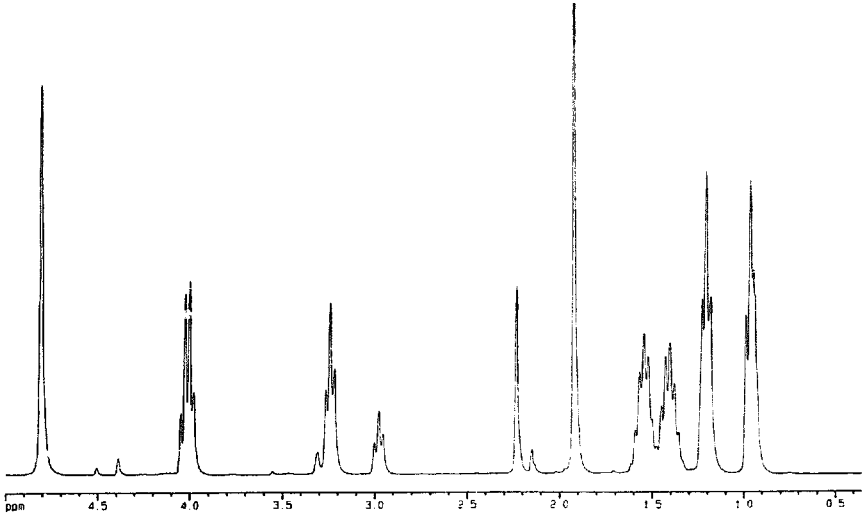


Fig. 1. ^{1}H NMR spectrum of AC in wet deuteromethanol solution stored in the dark at 4–8 °C for 10 days.

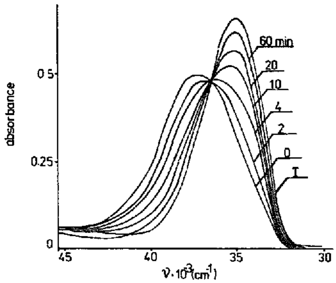


Fig. 2. UV spectra of AC (0.0647 g l^{-1}) in hexane solution: I, before irradiation; 0, after 30 min irradiation and 2, 4, 10, 20 and 60 min of reverse dark reaction.

solution confirm the specificity of the reaction (Figs. 2 and 3).

The hypsochromic shift of the maximum UV absorbance of AC, caused by irradiation with monochromatic light in hexane (18 nm) (Fig. 2) and methanol (7 nm) (Fig. 3) solution, corresponds to cis–trans isomerization. A similar difference in the UV spectra of the cis and trans isomers of methyl-cyclohexylaminocrotonate was observed by Huisgen et al. [10]. The observed photochemical cis–trans isomerization is reversible in the dark (Figs. 2 and 3), and the thermodynamically more stable cis isomer is formed (Scheme 1).

In contrast, only irreversible changes in the UV spectrum are observed on irradiation of a chloroform solution of AC (Fig. 4). The same behaviour is found for irradiated solutions of AC in CCl_4 and ethyl acetate. According to the IR spectra, these irreversible photochemical reactions do not correspond to the creation of the imino form. Comparable irreversible changes have been reported for the irradiation of PMAC and AC with polychromatic light ($\lambda > 300$ nm) [5] and were caused by photo-oxidation or photodimerization.

The photochemical reaction of AC in hexane solution was also studied by IR spectroscopy. A new absorption band resulting from irradiation is formed, with a maximum at 3448

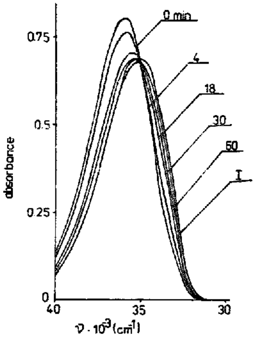


Fig. 3. UV spectra of AC (0.0647 g l^{-1}) in methanol solution: I, before irradiation; 0, after 30 min irradiation and 4, 18, 30 and 60 min of reverse dark reaction.

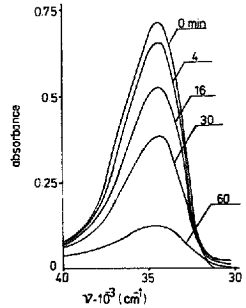


Fig. 4. UV spectral changes of AC in chloroform solution (0.0647 g l^{-1}) on irradiation for different times (no reverse dark reaction).

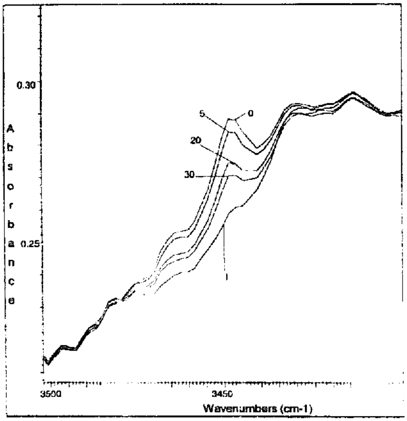


Fig. 5. IR spectra of AC (5.5 g l^{-1}) in hexane solution in the region 3500–3400 cm^{-1} measured in KBr cells: I, before irradiation; 0, after 30 min irradiation and 5, 20 and 30 min of reverse dark reaction.

cm^{-1} (Fig. 5), which corresponds to the absorption of the free amino group, as observed for methyl-cyclohexylamino-crotonate [10]. At the same time, the decrease in absorption at 1616 cm^{-1} and 1658 cm^{-1} (Fig. 6) is related to the decrease in the concentration of the cyclic conjugated system. The newly formed absorption band at 1701 cm^{-1} (Fig. 6) is related to the absorption of the free carbonyl group. The changes observed after scission on irradiation are reversible.

The above results show that the photochemistry of the enamino ester chromophore is very sensitive to the environment.

3.3. *Irradiation of PMAC film*

The irradiation of a PMAC film (cast on KBr or quartz plates) by monochromatic light (313 nm) results in significant changes in both the IR (Figs. 7 and 8) and UV (Fig. 9) spectra. After irradiation, it is possible to observe the dark reverse reaction for irradiation times of 120 and 15 min respectively (Figs. 7–9). However, this reversibility disappears at longer exposure times or on polychromatic (more intense) irradiation [5].

According to the ^{1}H NMR spectra in deuterochloroform, the structures of PMAC [6] and AC in the ground state are almost exclusively the enamino form (Scheme 1). The same

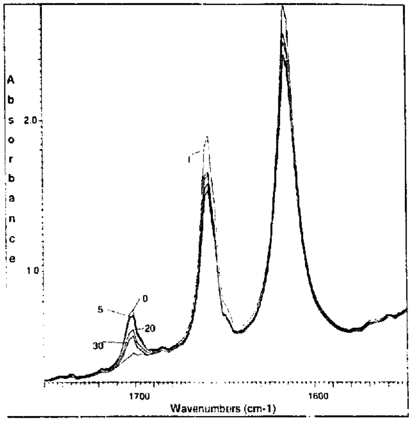


Fig. 6. IR spectra of AC (5.5 g l^{-1}) in hexane solution in the region 1750–1550 cm^{-1} measured in KBr cells: I, before irradiation; 0, after 30 min irradiation and 5, 20 and 30 min of reverse dark reaction.

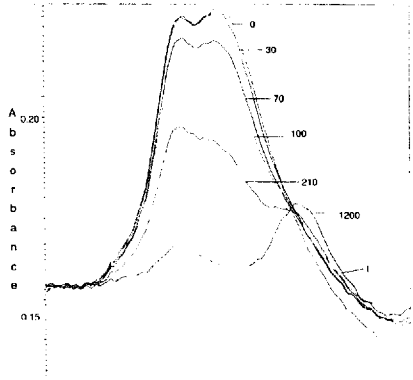


Fig. 7. IR spectra of PMAC film (4 mg per film) on KBr plate in the region 3500–3200 cm^{-1}: I, before irradiation; 0, after 120 min irradiation and 30, 70, 100, 210 and 1200 min of reverse dark reaction.

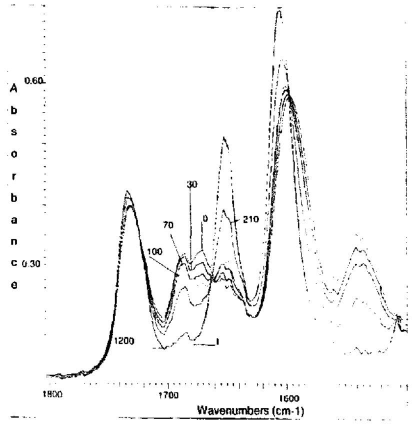


Fig. 8. IR spectra of PMAC film (4 mg per film) on KBr plate in the region 1800–1500 cm^{-1}: I, before irradiation; 0, after 120 min irradiation and 30, 70, 100, 210 and 1200 min of reverse dark reaction.

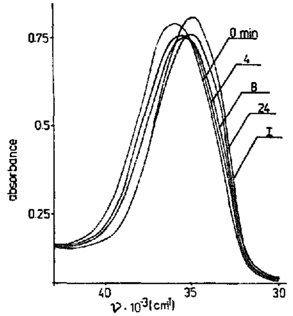


Fig. 9. UV spectra of PMAC film (0.14 mg per film) on quartz plate: I, before irradiation; 0, after 15 min irradiation and 4, 8 and 24 min of reverse dark reaction.

structure is also presumed in the PMAC film. The structures of PMAC and AC are stabilized in the cyclic cis form by both conjugation and hydrogen bonding. As in the similarly stabilized enol form of β-diketones [11], the absorption at 1600 cm^{-1} in the IR spectrum of PMAC (Fig. 8) is assigned to the ethylene double bond conjugated with carbonyl. The absorption at 1658 cm^{-1} corresponds to the carbonyl group. Both absorption bands belong to the conjugated cyclic cis isomer of enamine (Scheme 1).

The reversible changes observed in the irradiated PMAC film may be related either to cis–trans isomerization or enamine–imine tautomerization (Scheme 1). However, the IR and UV measurements provide evidence that, in this case, the latter photoreaction path does not occur.

The weak absorption of the intramolecular hydrogen bond at 3290 cm^{-1} is changed during the course of irradiation to the free, intermolecularly associated amino group absorbing in the region 3320–3430 cm^{-1} (Fig. 7). The free amino group formation can also be detected at 1530 cm^{-1}. The weak absorption at 1685 cm^{-1} is due to the formation of free carbonyl (no hydrogen bond) (Fig. 8). The decrease in the absorption of the conjugated cyclic system is very pronounced at 1600 and 1650 cm^{-1} (Fig. 8). In addition, the increase in the aliphatic ester absorption near 1730 cm^{-1} is very small and does not correspond to imine formation. Therefore the most probable transformation responsible for the primary photochemical reaction in this system is cis–trans isomerization (Scheme 1).

The changes in the UV spectrum (Fig. 9) are also consistent with cis–trans isomerization [10]. The isosbestic point of the reverse reaction provides evidence for its selectivity. However, the UV spectrum in Fig. 9 (incomplete intensity recovery) indicates that irradiation may result in photochemical reactions in addition to cis–trans isomerization [5]. A similar shift in the UV spectrum was observed for the photochemical cis–trans isomerization of compounds R–NHC(R′)=C(COR$_1$)(COR$_2$) [12]. In this case, the isomer formed is in the cyclic form and is stabilized by hydrogen bonding. The rate constants of the reverse reaction (3.2×10^{-4} s^{-1} for AC in hexane solution and 3.5×10^{-5} s^{-1} for the PMAC film) were evaluated from first-order plots (Fig. 10). The reason for the lower rate of the reverse reaction in the polymer film compared with that observed in *n*-hexane solution is probably the more restricted rotation around the C=C double bond in the solid polymer film.

The reverse dark reaction observed in the polymer film by UV measurements is faster (Fig. 9) than that observed by IR spectroscopy (Figs. 7 and 8). Optimum measurement of the reversible changes in the IR spectra (Figs. 7 and 8) requires irradiation times nearly ten times longer than in the case of UV measurements (Fig. 9). The different irradiation time (120 min vs. 15 min) is probably the reason for the different rate of the reverse reaction. One main factor affecting the

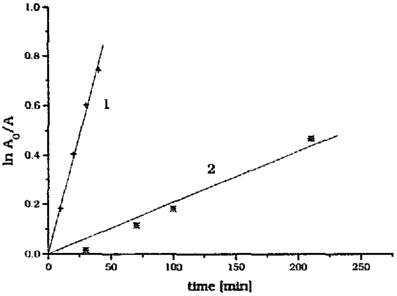


Fig. 10. First-order plot of reverse dark reaction for AC in *n*-hexane (1) and PMAC film (2). Values taken from Fig. 6 and Fig. 8.

reverse reaction is the degree of crosslinking, which is expected to increase with longer irradiation times. Therefore the degree of crosslinking is higher for the films used for the IR measurements than for those used for the UV measurements. The crosslinking results in restricted rotation around the C=C bond and therefore a longer time for the reverse dark reaction. Accordingly, only irreversible changes were observed when more intense polychromatic light was used for the irradiation of PMAC [5].

4. Conclusions

The primary photochemical reaction in a PMAC film and in AC in hexane or methanol solution is cis–trans isomerization. Reverse trans–cis isomerization proceeds in the dark.

Acknowledgements

The authors thank the Grant Agency of the Slovak Republic for partial support through grant no. 2/4005/97.

References

[1] H.H. Wasserman, S. Tearo, Tetrahedron Lett. 21 (1975) 1735.
[2] M. Ibrahim-Ouali, M.-E. Sinibaldi, Y. Troin, J.-C. Grain, Tetrahedron Lett. 37 (1996) 37.
[3] E.F. Panarin, V.V. Kopeikin, Makromol. Chem. 184 (1983) 701. S.J. Huang, O. Kitchen, L.J. Dibenedetto, Polym. Mater. Sci. Eng. 62 (1990) 804. S.T. Kim, H.S. Moon, M.S. Gong, Macromolecules 25 (1992) 7392.
[4] H.H. Wasserman, J.L. Ives, J. Org. Chem. 50 (1985) 3573.
[5] I. Lukáč, Cs. Kósa, U. Salz, N. Moszner, J. Photochem. Photobiol. A: Chem. 102 (1997) 259.
[6] N. Moszner, U. Salz, V. Rheinberger, Polym. Bull. 32 (1994) 412.
[7] P.J. Wagner, J. Am. Chem. Soc. 89 (1967) 2820.
[8] A. Gómez-Sánchez, M. Tena-Aldave, J. Chem. Soc. (C) (1968) 2570.
[9] C. Sandorfy, in: S. Patai (Ed.), The Chemistry of the Carbon–Nitrogen Double Bond, Wiley, London, 1970, p. 49.
[10] R. Huisgen, K. Herbig, A. Siegl, H. Huber, Chem. Ber. 99 (1966) 2526.
[11] R.M. Silverstein, G.C. Bassler, T.C. Morril, Spectrometric Identification of Organic Compounds, 5th ed., Wiley, New York, 1991, p. 115.
[12] B. Couchouron, J. Le Saint, P. Courton, Bull. Soc. Chim. Fr. (1983) 11–66.