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Photochemical changes of poly(methacryloyloxyethyl-3-*N*-*n*-butylaminocrotonate) at $\lambda > 300$ nm

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

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

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Abstract

The photo-oxidation reactions of poly(methacryloyloxyethyl-3-*N*-*n*-butylaminocrotonate) (PI) and the low-molecular-weight model compound ethyl-3-*N*-*n*-butylaminocrotonate (**II**) were investigated in solution and in film form.

On irradiation of an aerated solution of low-molecular-weight model compound **II** at $\lambda > 300$ nm, *N*-*n*-butylacetamide and ethyl glyoxalate are formed. Model compound **II** remains unchanged on irradiation in an inert atmosphere, in dilute solutions of hexane, acetonitrile or *n*-butanol and in the bulk. The diethyl ester of 2-butene-1,4-dicarboxylic acid is the major conversion product of the model compound during the sensitized photo-oxidation with rubrene in solution. In the same conditions, *N*-*n*-butylacetamide is formed from polymer PI in solution.

On irradiation of a PI film in air, a decrease in the UV absorption at 285 nm is observed. In the IR spectrum, a decrease is observed in the absorption at 1600 and 1650 cm^{-1}, which corresponds to the conversion of the cis form of the enamino ester stabilized by conjugation and hydrogen bonding. The irradiation of PI films leads to the formation of an insoluble crosslinked product and a small amount of *N*-*n*-butylacetamide. © 1997 Elsevier Science S.A. All rights reserved.

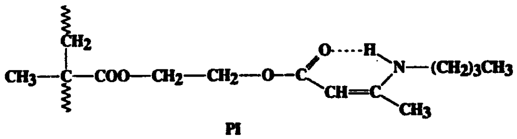
Keywords: Ethyl-3-*N*-*n*-butylaminocrotonate; Photo-oxidation; Poly(methacryloyloxyethyl-3-*N*-*n*-butylaminocrotonate); Singlet oxygen

1. Introduction

The controlled release of drugs or herbicides from polymeric substrates has attracted recent interest [1]. The hydrolysable polymeric aminovinyl carbonyl group of enaminone has been used to bind biologically active compounds [2]. Poly(amidoenamines) [3] and polyurethanes with enaminonitryl moieties in the chain [4] have been prepared for the same purpose.

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 [5]. Singlet oxygen takes part in the process. The reaction can also proceed in an "autosensitized" manner.

As the photo-oxidation of polymeric enamines has not been studied so far, we decided to investigate the photo-oxidation of poly(methacryloyloxyethyl-3-*N*-*n*-butylaminocrotonate) (PI) which has recently been synthesized [6].



PI

The photo-oxidation of the low-molecular-weight compound ethyl-3-*N*-*n*-butylaminocrotonate (**II**) was also studied in order to rationalize the photoreactions of the polymer.

2. Experimental details

2.1. Chemicals

Methacryloyloxyethyl-3-*N*-*n*-butylaminocrotonate (**I**) was prepared according to the method proposed by Moszner et al. [6]. Ethyl-3-*N*-*n*-butylaminocrotonate (**II**) was prepared by a similar route. The crude product was purified by distillation (boiling point (b.p.), 95 °C at 0.191 Torr). Its purity was checked by gas chromatography–mass spectrom-

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* Corresponding author. Tel.: +42 7 373448; fax: +42 7 375923.

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etry (GC–MS). ^{1}H nuclear magnetic resonance (NMR) ($CDCl_3$) δ (ppm): 0.94 (3H, t, $\mathbf{CH_3}CH_2CH_2CH_2$–), 1.25 (3H, t, $\mathbf{CH_3}CH_2$–), 1.40 (2H, m, $CH_3CH_2\mathbf{CH_2}CH_2$–), 1.54 (2H, m, $CH_3\mathbf{CH_2}CH_2CH_2$–), 1.9 (3H, t, CH_3–C=), 3.20 (2H, q, –$\mathbf{CH_2}$–NH–), 4.09 (2H, q, $CH_3\mathbf{CH_2}$–O–), 4.42 (1H, s, **H**–C=). Mass *m/e*: 185, 170, 156, 140, 110, 96, 70, 55, 42, 29, 14.

Polymer (PI) from I was prepared according to Ref. [6] by radical polymerization in a solution containing 2.73 g of the monomer, 33 mg of 2,2′-diazobis-isobutyronitrile (AIBN) and 5 ml of distilled tetrahydrofuran placed in a sealed tube under an argon atmosphere at 60 °C for 2 h. The polymer was precipitated into *n*-hexane. After triple precipitation from chloroform to hexane and drying, the yield of the polymer was 1.03 g (37.7%). $M_n = 37\,800$ and $M_w = 107\,000$ of the polymer were estimated by SEC using polystyrene calibration. PI became insoluble in organic solvents after storing in air in the dark at room temperature. Therefore PI was stored in chloroform solution under an inert atmosphere at −20 °C in the dark. A completely crosslinked film of PI was obtained after storage for 36 days in air in the dark, and showed no changes in its IR spectrum.

2.2. Equipment

The IR spectra were measured on Specord IR-80 (Zeiss, Jena, Germany) and Nicolet 400 (Nicolet, Germany) spectrometers. UV spectra were measured on a Specord M40 spectrometer (Zeiss, Jena, Germany). NMR spectra were recorded at 30 °C using an AM-300 (Bruker, Germany) instrument with tetramethylsilane as internal standard. The purity of the starting materials and the composition of the product were determined by gas–liquid chromatography combined with mass spectrometry using an SSQ 710 instrument (Finnigan, San Jose, USA) at 70 eV and 200 mA.

2.3. Irradiation

For irradiation at 25 °C, a merry-go-round equipped with a medium pressure mercury lamp (125 W, Tesla Holešovice, Prague) was used. The wavelength was higher than 300 nm and the distance of the samples from the centre of the lamp was 12 cm. An *n*-hexane solution of II (3 ml, 2.63 g dm^{-3}) was irradiated in closed cells, 1 cm thick. The oxygen was partially removed from some cells by purging with argon for 3 min.

Solutions (10 ml) of PI and II in chloroform ($c = 10$ g dm^{-3}) with and without a sensitizer (rubrene; in the case of II, also methylene blue; $c = 0.1$ g dm^{-3}) were irradiated under oxygen in quartz ampoules equipped with a magnetic stirrer. The same UV source as mentioned above ($\lambda > 300$ nm) was used and the distance of the ampoules from the source was 15 cm.

Thin films of PI were cast from $CHCl_3$ (0.5 ml) solution containing 0.14 mg of PI onto quartz glass (2.5 cm × 4 cm). Thick films were cast onto KBr plates (2 cm × 4 cm) using 0.8 ml of $CHCl_3$ solution containing 16 mg of PI. The irradiation of the films was performed in the merry-go-round apparatus as described above.

3. Results and discussion

3.1. Irradiation in solution

A decrease in absorption at 285 nm was observed in the UV spectrum of II irradiated in the presence of air (oxygen) in hexane solution by polychromatic light ($\lambda > 300$ nm) (Fig. 1). In the absence of oxygen, no changes in the spectrum of II were observed. The decrease in absorption at 285 nm was ascribed to a loss of double bonds. Two main products, *N*-*n*-butylacetamide and ethyl glyoxalate (Table 1), were determined by GC–MS (more than 90% conversion). The unsensitized photo-oxidation of II in hexane solution proceeds according to Scheme 1. This mechanism has been reported for other similar compounds [5]. The decrease in absorption at 285 nm in chloroform solution was faster in the presence of methylene blue as sensitizer (Fig. 2).

The irradiation of PI and the low-molecular-weight model compound II was carried out in chloroform, with or without rubrene as sensitizer, in a quartz cell under oxygen using light of $\lambda > 300$ nm. Rubrene was used instead of methylene blue

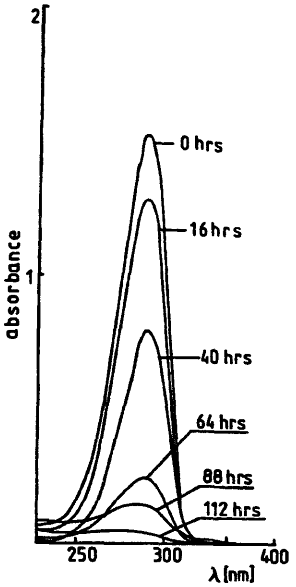
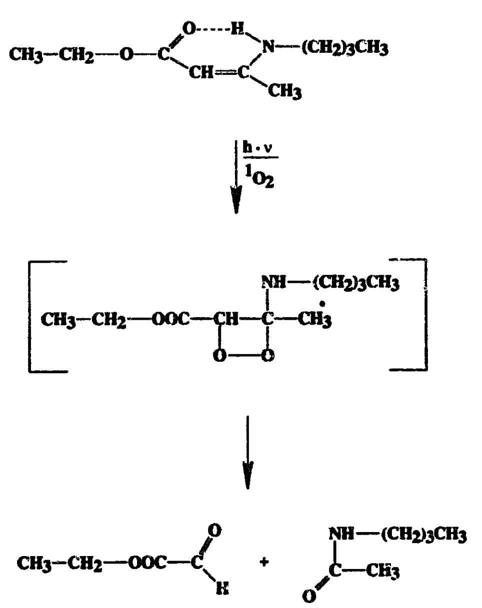


Fig. 1. UV spectra of II (2.63 g dm^{-3}) irradiated for different times in hexane solution (measured after 100 times dilution).

Table 1
Mass data of the main photochemical products

Product	*m/e*
N-*n*-Butylacetamide	115, 86, 72, 43, 30
Ethyl glyoxalate	102, 100, 73, 57, 29
Diethyl ester of 2-butene-1,4-dicarboxylic acid	172, 144, 116, 98, 57, 42



Scheme 1.

because of its solubility in PI. Because the time of irradiation was shorter and the light dose was smaller than in the former experiments, no changes were detected after 5 h of irradiation of a solution of model compound **II** in the absence of rubrene by GC–MS. However, 54% conversion was reached in the presence of rubrene after the same irradiation time. In this case, only a small amount of *N*-*n*-butylacetamide and ethyl glyoxalate was formed. The main product was the diethyl ester of 2-butene-1,4-dicarboxylic acid (three times higher concentration than the two minor products).

N-*n*-Butylacetamide was produced in much higher amounts by the irradiation of PI in solution in the presence of rubrene. Its concentration is comparable with that of the diethyl ester of 2-butene-1,4-dicarboxylic acid formed on irradiation of **II**. Because no crosslinking was observed, the irradiated polymer could be precipitated into hexane after partial evaporation of chloroform. A comparison of the IR spectra of the original and irradiated PI is shown in Fig. 3. Irradiation results in a decrease in the two peaks at 1600 and 1650 cm^{-1} and an increase in the absorption at 1740 cm^{-1}. As for the enol form of *β*-diketone [7] and the polymeric *β*-diketone poly(methacroyl acetone), the absorption at 1600 cm^{-1} is assigned to the ethylene double bond conjugated with the carbonyl group of the six-membered ring of the cis form, stabilized by hydrogen bonding. The absorption at 1650 cm^{-1} corresponds to the vibration of the C–O–CH$_2$ group attached to the conjugated system. The decrease in the double

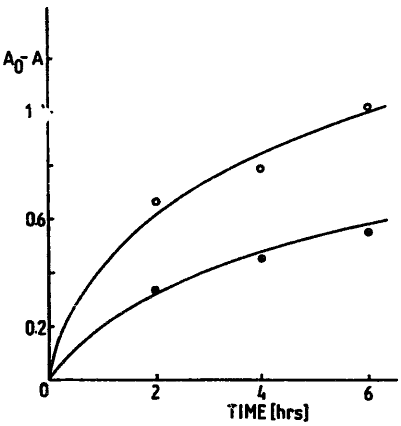


Fig. 2. Change in absorption at 235 nm of **II** (20.35 g dm^{-3}) irradiated in chloroform solution in air with (∘) and without (·) methylene blue (0.407 g dm^{-3}) (measured after 2000 times dilution).

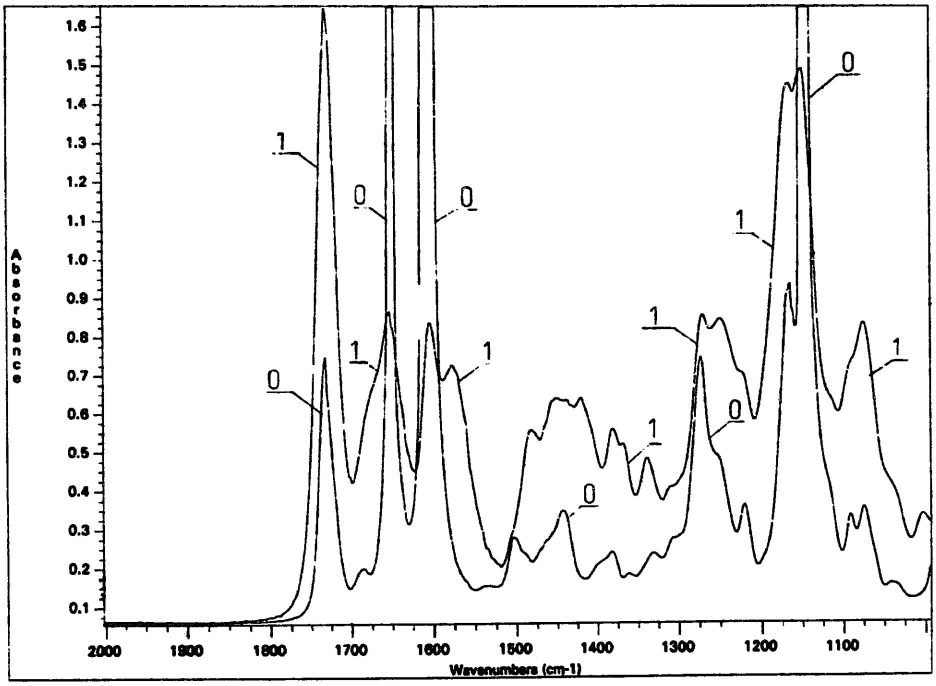
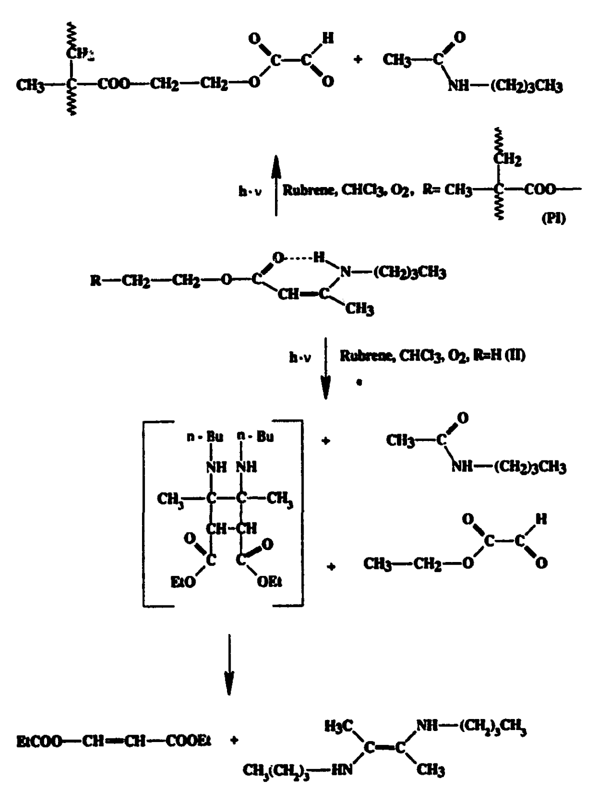


Fig. 3. IR spectra of unirradiated PI film (0) and PI film after sensitized photo-oxidation in chloroform solution (1). Films were cast from solution onto KBr plates.



Scheme 2.

bond content, i.e. the decrease in the 1600 and 1650 cm^{-1} absorptions, is combined with an increase in saturated ester groups (1740 cm^{-1}). Only a small amount of *N*-*n*-butylacetamide was detected in irradiated PI solution in the absence of rubrene.

The final products of the photosensitized reaction of PI and model compound **II** are shown in Scheme 2. Different products are obtained. Energy transfer from the sensitizer to polymer PI in solution is less effective than to low-molecular-weight compound **II**. The probability of double bond reaction with another double bond fixed on the polymer chain is also less effective. In the case of the polymer solution, the competitive reaction of energy transfer from the sensitizer to oxygen via the production of singlet oxygen is more favourable. The long lifetime of singlet oxygen favours its reaction with the polymer through the production of a dioxetane intermediate. This very unstable structure splits and gives *N*-*n*-butylacetamide and an aldehyde group bonded to the polymer. *N*-*n*-Butylacetamide can be separated from the polymer by precipitation. The aldehyde group is probably transformed to peroxy acid or acid under the conditions of photo-oxidation. A broad absorption of the hydroxyl stretching vibrations of the acid is observed in the IR spectrum at 3050–3650 cm^{-1}. The production of the diethyl ester of 2-butene-1,4-dicarboxylic acid from model compound **II** can be proposed through the production and decomposition of the cyclobutane ring. Similar ($2\pi+2\pi$) photocyclocondensation for adjacent thymine residues in the same strand of DNA has been observed [8]. Only the cis–syn dimer is formed. This dimer undergoes photocleavage to the starting structures in the presence of electron transfer sensitizers [8]. Regardless of the protection or decomposition of the cyclobutane ring in the intermolecular reaction in the polymer film, the result of reaction is the crosslinked product.

3.2. Irradiation of PI films

A decrease in absorption at 285 nm is observed in the UV spectrum of irradiated PI (Fig. 4). This high intensity band is associated with the π–π^* transition in the carbonyl group (conjugated with the ethylene double bond in the ring stabilized by hydrogen bonding) of the cis form of the enamino esters of PI and model **II**. The decrease is attributed to a loss of C=C double bonds. The time dependence of the reaction is shown in Fig. 5.

The IR spectrum of the irradiated polyenamine film shows a decrease in absorption at 1600 and 1650 cm^{-1}. The absorption increases at 1740 cm^{-1} and the formation of a new small absorption band at 1715 cm^{-1} (Fig. 6) is observed.

The decrease in absorption at 1600 cm^{-1} corresponds to a loss of double bonds. The parallel growth of the saturated ester absorption at 1740 cm^{-1} is observed. The absorption at 1715 cm^{-1} corresponds to the vibrations of the carbonyl

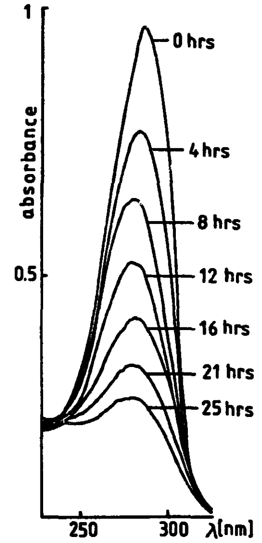


Fig. 4. UV spectra of unirradiated PI film and PI films irradiated for different times (in air) (0.14 mg on quartz glass).

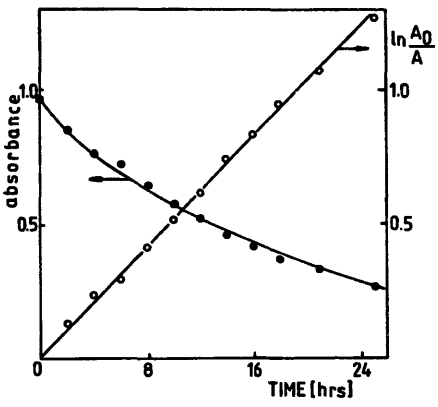


Fig. 5. Time dependence of the absorption of PI.

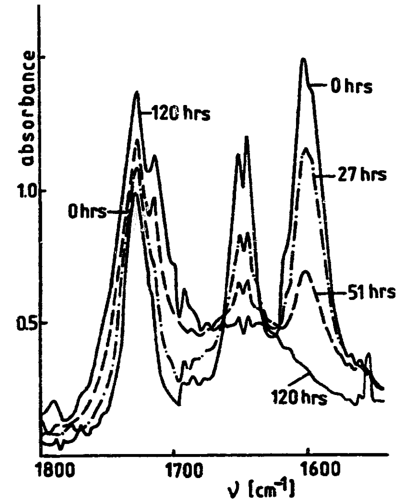


Fig. 6. IR spectra of unirradiated and irradiated (in air) PI (20 mg) on KBr plates.

groups formed via photo-oxidation. In the presence of rubrene, the changes are greater.

Only a small amount of product (8 wt/wt.%) can be extracted by chloroform from 92 h irradiated PI films. The major product identified in the extract was *N-n*-butylacetamide as in the case of irradiated **II**. The extracted amount represents less than 18% of the theoretical value according to Scheme 1.

In the polymer film, there is an increased concentration of all groups. An increased concentration favours condensation reactions. Dimerization and polymerization of the double bound of crotonate can be suggested as the main reactions. Polymerization can be initiated by dioxetane intermediate decomposition. The extent of the condensation reactions will also be increased by the possible quenching of singlet oxygen by amines [9], which lowers the extent of photo-oxidation. Dimerization and photo-oxidation can be sensitized (rubrene).

4. Conclusions

Primary intermolecular $2\pi+2\pi$ cycloaddition with cyclobutane ring production is a major photochemical reaction. This reaction is responsible for the consumption of double bonds and the crosslinking of the PI film. This reaction can be sensitized.

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