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Irradiation of camphorquinone in glassy polymer matrices in the absence and presence of molecular oxygen

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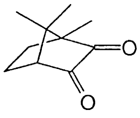
Abstract

The reaction of camphorquinone (CQ) upon irradiation (>370 nm) and formation of camphoric anhydride and camphoric diacid have been followed in aerated and deaerated polystyrene (PS), poly(methyl methacrylate) (PMMA), bisphenol A polycarbonate (PC), and bisphenol A polysulfone (PSF) films using infrared spectroscopy. In deaerated PS the formation of reduction adducts analogous as in toluene and/or *p*-xylene solution was observed. Contrary to observations for the corresponding photo-oxidation of benzil in polymer films, no diacyl peroxide was detected. The rate of CQ consumption does not show a marked dependence on the type of polymer matrix, the bulk concentration of CQ, or the film thickness, but it does increase significantly with larger oxygen concentrations at larger light intensity used. A decrease of PS molecular weight accompanies loss of CQ. The degree of polymer degradation was highest in an argon atmosphere and lowest in an oxygen atmosphere.

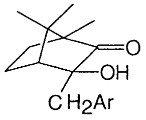
Keywords: Camphorquinone; Polymer film; Photochemistry; Photo-oxidation; Photo-reduction

1. Introduction

Camphorquinone (CQ), in the presence of H-atom donors like amines, is known to be an effective photo-initiator for curing acrylate- and methacrylate-based dental restorative resins [1]. However, the specific mechanism of photo-initiation by CQ remains unclear despite the rather extensive studies of its photochemistry in the presence or absence of atmospheric oxygen [2–4]. Irradiations in oxygen-free solutions of benzene, carbon tetrachloride, *t*-butyl alcohol, methanol, and acetone are reported to produce no discernible loss of CQ while in toluene or *p*-xylene, 1:1 adducts with solvent molecules (**1** and **2**) are the major photoproducts [5–7].



CQ



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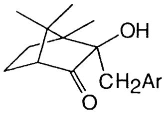

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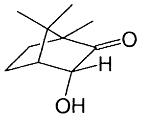
Irradiations of CQ in the presence of molecular oxygen yield products whose structures depend on the specific nature of the solvent. When the solvent has easily abstractable H-atoms, such as methanol or 2-propanol, mixtures of acyloins as *endo*-3-hydroxycamphor (**3**) and *endo*-2-hydroxyepicamphor (**4**), as well as various camphoric acid esters (**5**), are formed [4]. In xylene, the only products obtained were **6** and camphoric diacid **7** [7]. In solvents lacking easily abstractable H-atoms, such as carbon tetrachloride and *t*-butyl alcohol, camphoric anhydride (**6**) is the main photoproduct and in benzene, the isomeric campholactones (**8** and **9**) are obtained in largest yields [4].



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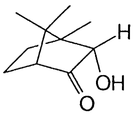

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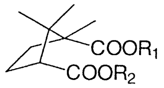

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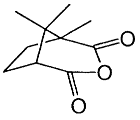

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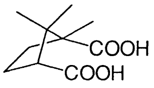

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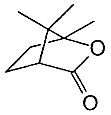

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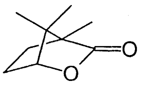

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In benzene, the presumed intermediate, predicted to formation of lactones, is camphordiacyl peroxide (**12**), formed by reaction between CQ and molecular oxygen [4]. Preliminary attempts to prepare **12** in solution have not been successful [4]. In previous work, we have determined that

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the corresponding peroxide of benzil, another 1,2-diketone, is formed almost quantitatively upon irradiation in aerated glassy polymer films, but not in liquid solutions [8,9].

The striking differences observed for the excited state reactions of CQ in solutions in the presence and absence of molecular oxygen and our surprising results with benzil have led us to investigate the photochemistry of CQ in glassy matrices consisting polystyrene (PS), poly(methylmethacrylate) (PMMA), bisphenol A polycarbonate (PC), and bisphenol A polysulfone (PSF) films. Irradiations at $\lambda > 370$ nm, to ensure initial excitation to the n–π^* singlet state, have been conducted in the presence and absence of molecular oxygen.

2. Experimental

2.1. Materials

All solvents and hydrogen peroxide were analytical grade and used without further purification. CQ (Aldrich), PS (Vestyron N, Chemische Werke, Huls, Germany), PMMA (Chemické Závody, Žilina, Slovak Republic), PSF (Udel, P-3500, Amoco Performance Products, USA), and PC (Lexan, GE, USA) were used as received.

2.2. Preparation of camphoric diacid (7)

To a mixture of 33 mg (0.2 mmol) of CQ and 180 mg (4.5 mmol) of NaOH 1.5 ml of 30% H_2O_2 was added dropwise. After 5 min, the solid CQ dissolved. The solution was maintained at ambient temperature during 2 h and then poured into cold 5% aqueous NaOH, and extracted with diethyl ether. The aqueous layer was acidified with dilute HCl, extracted with diethyl ether, and the ether layer was dried, reduced to residue, and recrystallized from ether:chloroform to yield 34 mg (85%) of white crystals, mp 189–194 °C ([11] 189–191 °C). IR (cm^{-1}): 1701(s), 1602(m), 1377(m), 1247(w), 1275(w) and 1125(w) [10].

2.3. Preparation of camphoric anhydride (**6**)

30% H_2O_2 (4 ml) was added dropwise to a solution of 1 g (6.02 mmol) of CQ in 6 ml of acetic acid. The solution was allowed to stand until it became colorless (3 h) and then water was added. The precipitate was filtered, washed with water, and dried to afford 0.74 g (68%) of colorless needles, mp 217–222 °C ([7] 221–223 °C). IR (cm^{-1}): 1810(s), 1767(m), 1126(m), 1040(m), 995(m), 982(m), 942(w) and 566(w) [12].

2.4. Irradiations and analytical procedures

Aerated films were irradiated ($\lambda > 370$ nm) at ambient temperature in merry-go-round apparatus using output of a 125 W medium-pressure mercury lamp placed in a water-cooled Pyrex jacket and the glass filter 73087112 (Carl Zeiss, Jena, Germany). The distance between the films and the lamp was 8 cm. In some experiments, primarily for irradiations in molecular oxygen or argon atmospheres, more intense radiation from a medium-pressure mercury arc ($\lambda >$ 400 nm) in a Spectramat® apparatus (Ivoclar A.G., Schaan, Liechtenstein) was used in combination with a UV CL SR HPR plastic film filter (LLumar, USA).

Polymer films were cast from benzene solutions (1 ml containing 20 mg of polymer and 2 mg of CQ, except as noted otherwise) on 2.5 cm × 4 cm glass plates. Polystyrene films of various thicknesses were prepared by casting from benzene solutions (1 ml containing 2 mg of CQ and 20, 40, 60, 80 or 100 mg PS) on 2.5 cm × 4 cm glass plates. A polymer film containing camphoric diacid was prepared by casting from 1 ml of benzene and 0.3 ml of diethylether solution containing 20 mg of polystyrene and 1 mg of camphoric diacid. Plates were covered by a Petri dish to slow solvent evaporation. This procedure resulted in films with good optical quality. Residual solvent was removed by drying films under vacuum to constant weight at room temperature. The self-supporting polymer films containing CQ were mounted in frames made of aluminum foil after being separated from the glass plates by dipping the assemblies into distilled water.

Films irradiated in oxygen atmospheres were placed into glass tubes, evacuated at 13 Pa, filled with oxygen gas for 2 min (three pump-fill cycles), and sealed. Films irradiated under argon atmospheres were prepared in an analogous fashion.

For GC–MS analyses JMFD 100, JEOL spectrometer was used. For analyses of low-molecular product in irradiated PS film containing CQ the films were dissolved in chloroform and the PS was removed by filtration after precipitation with methanol. The filtrate was concentrated under reduced pressure and the residue was dissolved in hexane and injected.

Emission spectra were recorded on a Perkin-Elmer MPF-4 spectrofluorimeter at 470 nm excitation wavelengths. IR spectra were measured on a Nicolet 400 FT-IR spectrometer.

3. Results and discussion

3.1. Irradiations in merry-go-round apparatus

Decreases in absorbance of the dicarbonyl group of CQ (1773 and 1756 cm^{-1}) and increases in absorbances of carbonyl groups of camphoric anhydride (**6**) at 1810 and 1767 cm^{-1} and of camphoric diacid (**7**) at 1701 cm^{-1} were monitored by FT-IR during irradiations in polymer matrices in the presence of air (Figs. 1–4). Loss of CQ was followed most conveniently during kinetic measurements at 1756 cm^{-1}. The assignments of the absorptions bands in infrared spectra are based on the spectra of independently prepared compounds doped in PS films at different ratios. On this basis, the **6**:**7** photoproduct ratios in PS at room temperature are estimated to be 3:2.

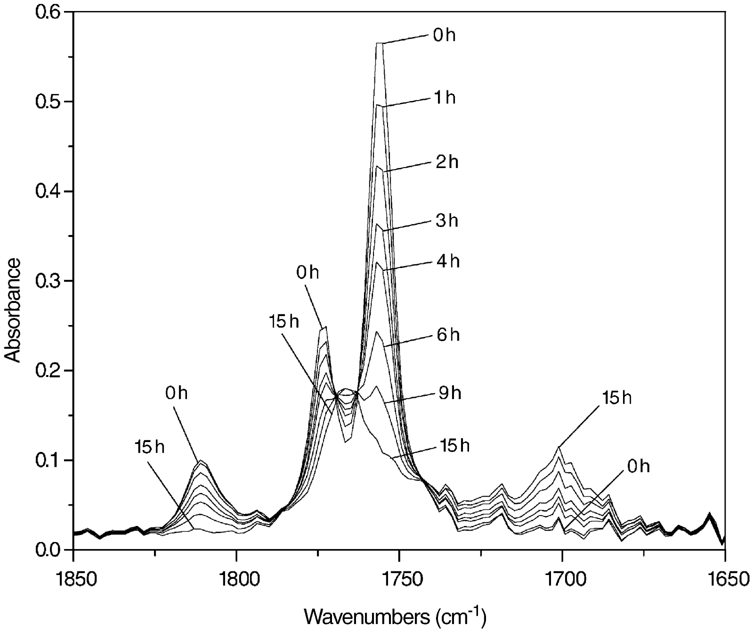


Fig. 1. FT-IR spectra of CQ in an aerated PS film (2 mg CQ/20 mg PS) after irradiation in merry-go-round apparatus for the indicated periods.

After exposure of the irradiated film to temperature 90 °C during 2 h, no change was observed by infrared spectroscopy. Thus, it signifies that no thermally unstable eight-member ring camphordiacyl peroxide, which FT-IR vibration maxima $\nu_{(C=O)}$ would be expected to be in area about 1800 cm^{-1}, was present after irradiation.

By GC–MS analyses, a 1:5 ratio of two low-molecular mass products is formed upon irradiation of aerated PS films containing CQ. The identity of the major product, camphoric anhydride (MS: 183(2) (M + H), 138(43), 123(19), 110(13), 95(100), 83(42), 69(49), 55(34), 41(29)), was confirmed by comparison with the mass spectrum of the independently prepared material. The highest mass fragment of the minor unidentified product was 341. Camphoric diacid was not detected by GC–MS analysis. Reason is problem in its isolation from polymer film. Camphoric diacid is insoluble in solvents like $CHCl_3$, in which the polymers are soluble. Therefore,

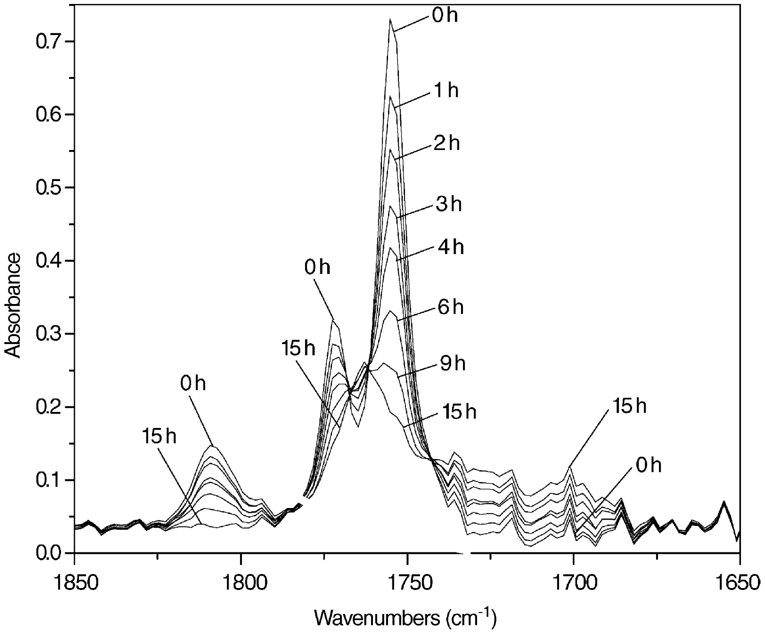


Fig. 2. FT-IR spectra of CQ in an aerated PSF film (2 mg CQ/20 mg PSF) after irradiation in merry-go-round apparatus for the indicated periods.

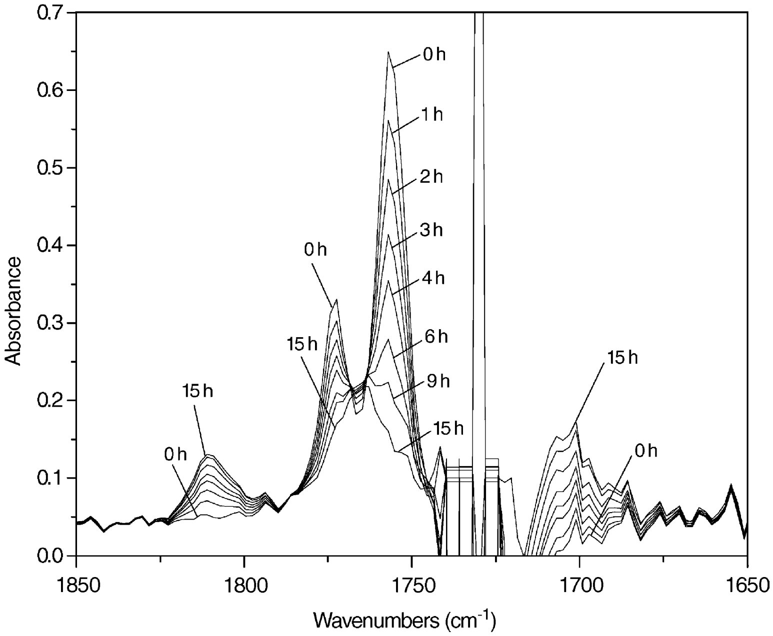


Fig. 3. FT-IR spectra of CQ in an aerated PMMA film (2 mg CQ/20 mg PMMA) after irradiation in merry-go-round apparatus for the indicated periods.

FT-IR is more reliable method for estimating photoproducts ratio.

Films at 2 mg CQ/20 mg polymer concentration in various film matrices were irradiated simultaneously in the merry-go-round apparatus to provide an equal doses with time for all samples. In all cases, formation of **6** and **7** was observed (Figs. 1–4). Changes of $\ln A/A_0$ (where A and A_0 are the CQ absorbances at 1756 cm^{-1} at time = t and 0, respectively) with time are plotted in Fig. 5. As seen there and in Table 1, the pseudo-rate constants for CQ consumption are approximately the same in all of the polymer matrices and change very slightly when the initial CQ concentration is doubled. This indicates that in the presence of molecular oxygen, the composition of polymer does not influence CQ consumption and photo-oxidation of CQ proceeds mainly.

The influence of CQ concentration (over a 10-fold range) on the rate of its consumption in PS films was followed also by maintaining the rate of photons absorbed constant.

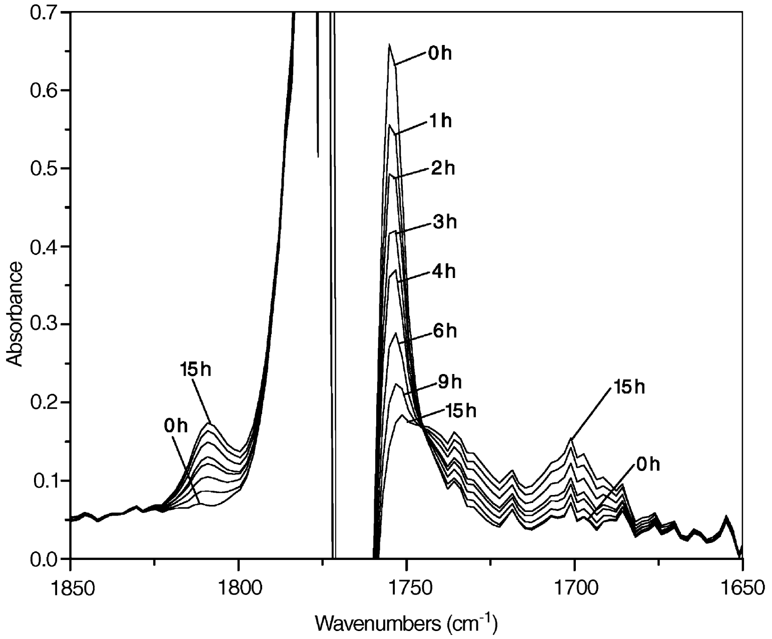


Fig. 4. FT-IR spectra of CQ in an aerated PC film (2 mg CQ/20 mg PC) after irradiation in merry-go-round apparatus for the indicated periods.

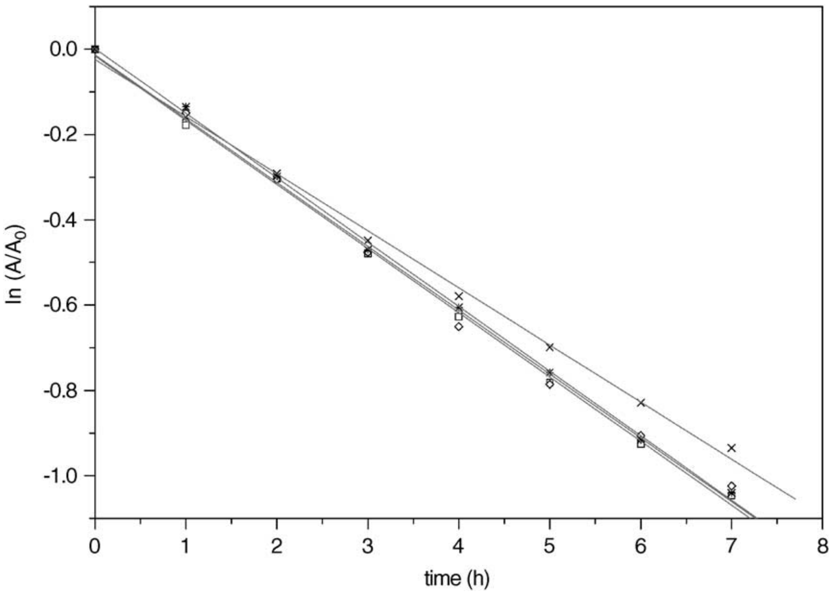


Fig. 5. Plots of absorbance changes at 1756 cm^{-1} upon irradiation of CQ-doped polymer films (2 mg CQ/20 mg polymer) in a merry-go-round apparatus for various periods: (×) PSF; (◇) PMMA; (✳) PS; (☐) PC.

Table 1
Concentration of molecular oxygen in the air equilibrated polymer matrices [8], corresponding coefficient of diffusion [8] and rate constants for CQ consumption (k) upon irradiation in aerated polymer films (20 mg per film)

Matrix	$[O_2]$ (mol dm^{-3})	D ($cm^2\,s^{-1}$)	k (h^{-1})		
			2 mg CQ per film	4 mg CQ per film	4 mg CQ per film[a]
PMMA	0.29×10^{-3}	0.38×10^{-7}	0.150	0.159	2.58
PS	1.64×10^{-3}	1.1×10^{-7}	0.148	0.163	4.44
PSF	2.27×10^{-3}	0.44×10^{-7}	0.131	0.119	2.52
PC	4.78×10^{-3}	0.21×10^{-7}	0.151	0.187	6.12[b]; 2.4[c]

[a] Irradiated in Spectramat®.
[b] 0–5 min of the irradiation.
[c] After 10 min of irradiation.

More dilute doped films were made correspondingly thicker (i.e. so that the “area” concentration of CQ was always 2 mg/10 cm^2 and that of PS 20–100 mg/10 cm^2, so absorbances at the irradiation wavelengths were the same at all concentrations). The films were irradiated simultaneously in the merry-go-round apparatus and the rates of CQ consumption were estimated as before from FT-IR spectra. The deviation in the values for the pseudo-rate constant for CQ consumption, $k = 0.23 \pm 0.03\,h^{-1}$ (Table 2), over the 10-fold change in concentration was within the limits expected for precision. Therefore, we conclude that CQ concentration and thickness (as they pertain to the availability of oxygen molecules during irradiations) of PS films do not influence the rate of CQ consumption within the range investigated.

Based on the results above, it is unlikely that aggregation of CQ molecules (or lack thereof) or self-quenching affects their conversion to the photo-oxidized products. Furthermore, FT-IR analyses of CQ crystals irradiated for 20 days between two glass plates in air indicate the formation of **6** and **7** in a 3:2 ratio, as observed from irradiations in aerated PS films.

Table 2
Pseudo-rate constants for CQ consumption (k) in aerated PS films as a function of bulk CQ concentration[a]

k (h^{-1})				
2 mg CQ/20 mg PS	2 mg CQ/40 mg PS	2 mg CQ/60 mg PS	2 mg CQ/80 mg PS	2 mg CQ/100 mg PS
0.256	0.221	0.202	0.266	0.209

[a] Correlation coefficients (r) are 0.9992–0.9997.

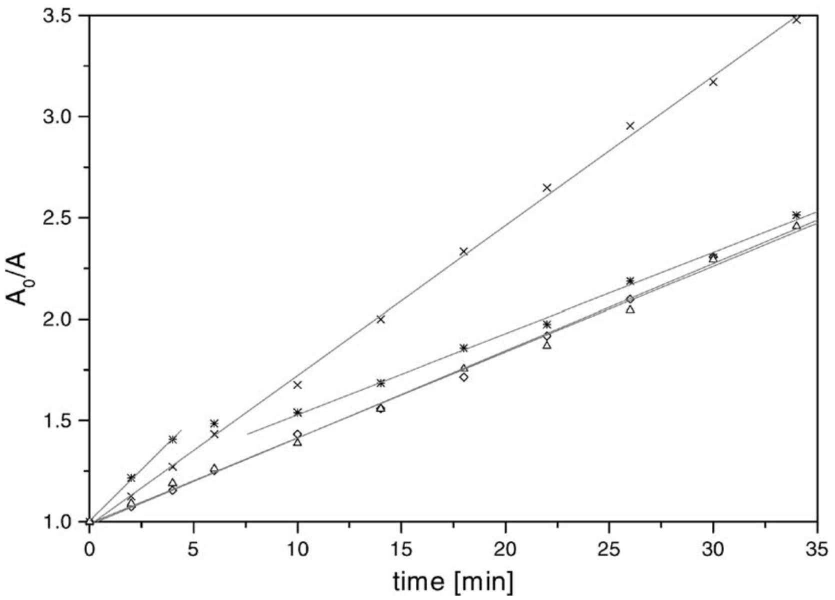


Fig. 6. Plots of absorbance changes at 1756 cm^{-1} upon irradiation of CQ-doped polymer films (4 mg CQ/20 mg polymer) in a Spectramat$^{\circledR}$ apparatus on air for various periods: (×) PS; (◇) PMMA; (✱) PC; (△) PSF.

3.2. Irradiations in a Spectramat$^{\circledR}$

The rate data in Fig. 6 (and Table 1) were obtained when films containing 4 mg CQ/20 mg polymer were irradiated with the more intense photon source in Spectramat$^{\circledR}$ and in air. As expected, the corresponding rate constants are more than 1 order of magnitude higher than calculated with the lower-intensity medium-pressure lamp, but unlike the experiments with the lower-intensity, the achieved rate constants are of the second order. In the case of PC matrix, two different rate constants were obtained. The first, at the beginning, is higher and the second, from the 10 min of progress of irradiation, is lower (Fig. 6, Table 1). The irradiation in Spectramat$^{\circledR}$ allows to obtain additional information about the potential depletion of oxygen during conversion of CQ. With higher intensity of light increases concentration of CQ in the excited state. However, the amount of oxygen in polymer film and the rate of diffusion of oxygen into the film are limited by the type of polymer used. By the taking into the account this two facts, the rate of the CQ consumption could depend on the type of polymer matrix. The concentrations of molecular oxygen in the air-equilibrated polymer matrices $[O_2]$ and corresponding coefficients of diffusion D are in Table 1. When the first (higher) rate constant for PC is taking into account, the rate constants for CQ consumption increase with increasing equilibrium concentrations of molecular oxygen in the polymer matrices (Table 1). There is also correlation between the rates constants for CQ consumption and coefficients of diffusion, when the second (lower) rate constant is taking in account for PC matrix. Exception in both cases is just for PSF, where, like in the previous irradiations of CQ with the lower intensity lamp, the rate constant is lower than it would be expected.

The lack of a clear relationship between the rates of CQ loss and oxygen diffusion coefficients suggests that the local concentrations of oxygen in all of the films remain adequate to scavenge the key photochemical intermediates leading to **6** and **7** throughout the experiments. The initial CQ concentration in these experiments, ca. 1.2 mol/kg polymer, is ca. 250–4000-fold larger than the molecular oxygen concentrations in each of the films. However, given the protracted periods necessary to convert CQ to products and the large diffusion coefficients for oxygen, the initial and steady-state concentrations of molecular oxygen would remain almost the same throughout the irradiations so the diffusion of molecular oxygen should not be a limiting factor. From our observation this seems to be right in the case of irradiation with lower intensity source, where the rate constants of CQ consumption are of pseudo-first order and do not depend on type of polymer matrix and so on the oxygen concentration (Fig. 5, Table 1). However, in the case of irradiation in Spectramat$^{\circledR}$, the rate constants of CQ consumption fit dependence suits better to second-order plot (Fig. 6), that means that the rate constants probably depend on the oxygen concentration. The two different rate constants for PC matrix would be caused with the high equilibrium concentration of molecular oxygen in the beginning of irradiation. However, after 5 min of irradiation the oxygen concentration falls down and it is controlled with the rate of oxygen diffusion to the polymer film. Because, the coefficient of oxygen diffusion for PC is too low, so concentration of oxygen, and therefore also the rate constant of CQ consumption in the second period of irradiation, is lower than that in the beginning of the irradiation. For PMMA and PS, starting equilibrium concentrations of molecular oxygen are lower and can be maintained also during irradiation, because the diffusion coefficients of molecular oxygen are higher as compared with PC.

The lower rate in PSF is consistent with (and more marked than) the trend observed using the lower intensity lamp source. The lower rate does not appear to be a consequence of the small population of easily abstractable H-atoms in PSF because an equally small population is expected in PC, where the rate of CQ consumption does not appear to be ‘abnormal’. The data indicate that PSF affects the photo-physical properties of CQ differently than do the other polymers, making its quantum yield for conversion lower than in the other three polymer matrices. Consistent with this hypothesis, the lowest quantum yield for fluorescence from CQ in the PSF films is found (vide infra). Similarly, physical quenching of CQ excited state with other sulfur compounds (with organic sulfides), was observed [1].

Irradiations of CQ have also been conducted comparatively in PS films saturated with air, molecular oxygen, and argon. FT-IR spectra of films before and after 9 min irradiation periods are shown in Fig. 7. They can be compared with FT-IR spectra obtained after 2 h of irradiation in Fig. 8. As expected, the CQ consumption increases with oxygen concentration, which is in accord with results observed in the irradiation of CQ in xylene solution [7]. It is evident, also, that the product compositions depend on molecular oxygen concentration; mainly increase of the amount of oxidation products with increasing concentration of oxygen. But also in the experiment conducted under an argon atmosphere, small amounts of oxidation products—camphoric acid and camphoric anhydride (probably from traces of molecular oxygen that did not diffuse from the films as they were purged with argon)—can be discerned.

After 2 h of irradiation of CQ in PS in argon atmosphere the completed depletion of CQ was reached (Fig. 8). Beside oxidation products in air and oxygen, in argon atmosphere also a new broad peak at 1744 cm^{-1} and weak one at 1781 cm^{-1} is seen in FT-IR spectra (Fig. 8). These peaks are consistent with the presence of photo-reduced CQ products [5]. The intensity of the 1744 cm^{-1} peak is much smaller in the air-saturated film and negligible in the molecular oxygen-saturated one. The irradiated CQ in PS film in argon atmosphere was dissolved in chloroform and polymer precipitated in methanol. The polymeric part was cast into a film from chloroform. To the in-methanol-soluble part (concentrated) was added 20 mg of fresh PS and cast into a film from chloroform. FT-IR spectra of these three films were similar (containing peaks at 1744 cm^{-1}). GC–MS analyses of an aliquot of the methanol-soluble part showed various unidentified products that contain mass fragments characteristic of both camphoric (*m*/*e* 139, 123, 111, 95, 83, 69, 55, 41) and styryl groups (*m*/*e* 105, 91, 77). They were probably formed by combination of camphoric radicals and low-molecular polystyrene radicals.

The molecular weight of PS in CQ-doped PS films was also determined by viscometry before and after irradiation for various periods and under different atmospheres (Table 3). The molecular weight decreases are largest after the longest irradiation times and at smallest molecular oxygen concentration. The molecular oxygen inhibits PS degradation by >400 nm radiation in the presence of CQ. First step in PS degradation should be H-abstraction from

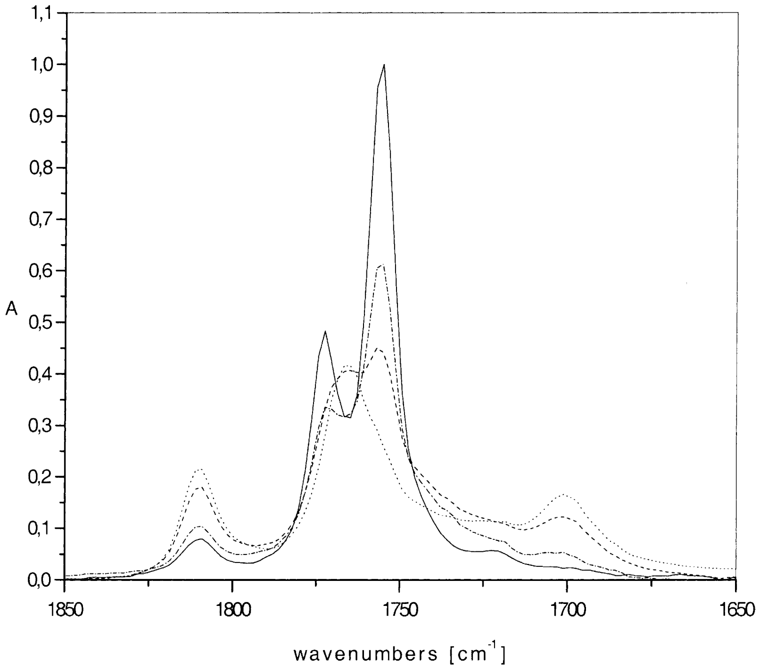


Fig. 7. FT-IR spectra of CQ-doped PS films (2 mg CQ/20 mg PS) prior to irradiation (—) and after irradiation in a Spectramat® apparatus for 9 min under argon (-·-), air (- - -) and molecular oxygen (···).

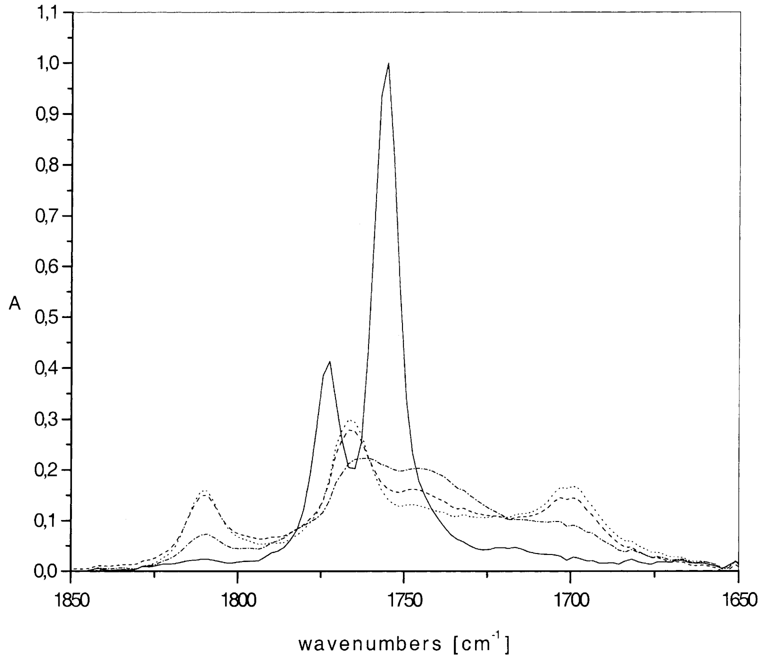


Fig. 8. FT-IR spectra of CQ-doped PS films (2 mg CQ/20 mg PS) prior to irradiation (—) and after irradiation in a Spectramat® apparatus for 2 h under argon (-·-), air (- - -) and molecular oxygen (···).

PS-backbone, most probably from the benzylic group, with excited triplet state of CQ and/or with intermediates radicals of CQ photo-oxidation. From the effect of oxygen concentration, its possible conclude, that for degradation of PS is responsible mainly (or exclusively) triplet state of CQ.

3.3. *Emission spectra*

The emission spectra of CQ in various liquid solutions and in the four polymer matrices (Fig. 9) have been measured. No excimer-like emission was observed in any of the media. Spectra in CCl_4, cyclohexane and methanol solutions are like those published previously [13], but our relative phosphorescence intensities are weaker, probably as a result of solvent impurities and residual oxygen acting as quenchers [8,14] of both fluorescence and phosphorescence. Emissions, predominantly fluorescence quantum yields from CQ, calculated relative to anthracene [15] (Table 4), are 1 order of magnitude higher in the polymer films than in liquid solutions. Reason is known higher stabilization of excited state of CQ with polymer matrix, when compared with solution. Only in PMMA is phosphorescence from CQ (shoulder near 560 nm) evident. The somewhat lower quantum yield measured in PSF is indicative of specific interactions between the excited singlet state of CQ and the polymer

Table 4
Wavelength of CQ absorption (λ_a) and emission (λ_{em}) maxima and emission quantum yields (Φ_E; $\lambda_{ex} = 472$ nm) in various media

Medium	λ_a	λ_{em}	Φ_E[a]
Chloroform	474	507	
Cyclohexane	481	509	0.0019
Methanol	467	508	0.0016
PC	468	518	0.046
PMMA	470	523	0.024
PS	472	526	0.023
PSF	472	525	0.01

[a] Relative to anthracene.

Table 3
Limiting viscosity number (η) and viscosity molecular weight (M_v) of CQ-doped films (2 mg CQ/20 mg PS) before and after irradiation in a Spectramat® apparatus under various atmospheres for different periods

	Unirradiated	Atmosphere		
		Molecular oxygen	Air	Argon
η	0.805	0.719[a] (0.735)[b]	0.6745[a] (0.6815)[c]	0.540[a]
M_v	213900	182900[a] (188600)[b]	167600[a] (169950)[c]	123300[a]

[a] Irradiation period: 2 h.
[b] Irradiation period: 9 min.
[c] Irradiation period: 40 min.

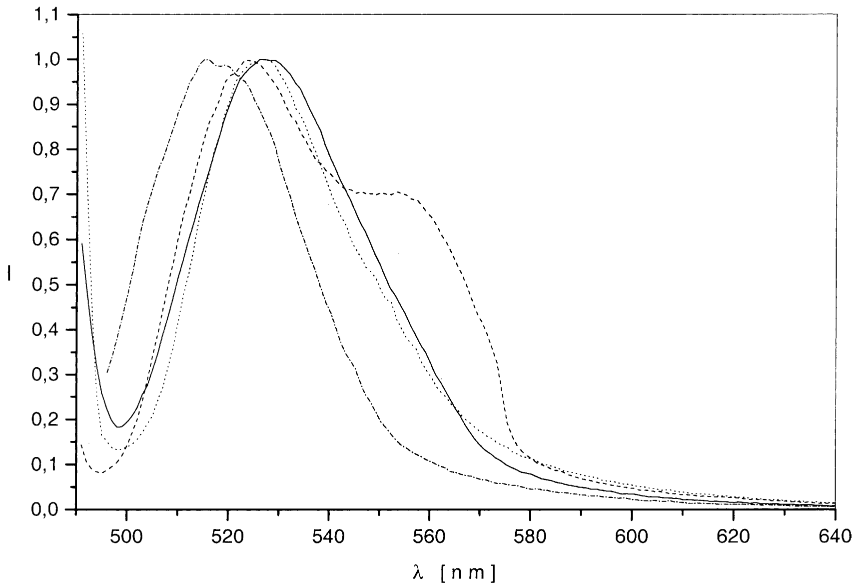


Fig. 9. Emission spectra of CQ (4 mg CQ/20 mg polymer) in aerated (—) PS, (- - -) PMMA, (- · -) PC and (· · ·) PSF films.

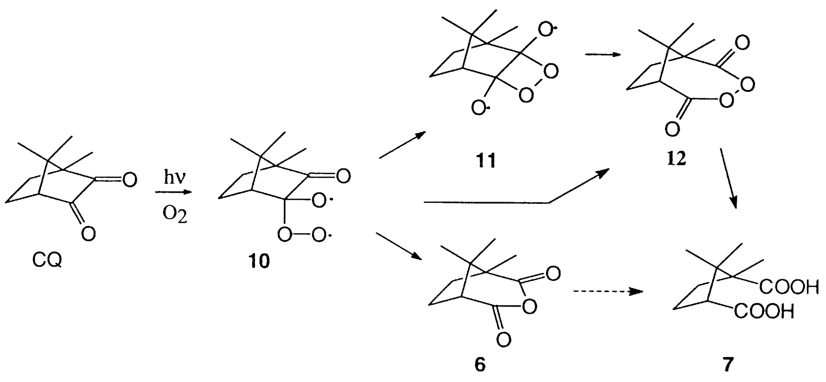
matrix, possibly involving SO_2 groups. This effect has been discussed above with respect to the lower efficiencies of CQ photoreactions in PSF.

There is correlation between emission quantum yields in various polymer matrices and rate constants (estimated from the beginning of irradiation) of consumption of CQ irradiated in various polymer matrices in Spectramat$^{\circledR}$. The rate constants increase with increasing quantum yields of emission. Exception is only for PMMA, which have Φ_E higher than it would be expected. The reason is that the value of Φ_E for PMMA contains besides fluorescence also phosphorescence, which was not observed for other polymers. So real value of fluorescence quantum yield for PMMA is smaller. It could prod that the CQ reacts with oxygen in its excited singlet state and ISC to triplet state decreases quantum yield of reaction (and the rate constant of CQ consumption). However, this way seems to be not probable, because it was reported [16] that CQ reacts in its triplet state.

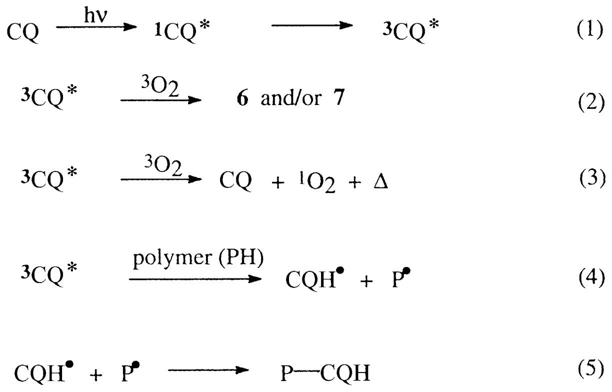
Agreement with the correlation between fluorescence quantum yields and rate constants of reaction from triplet state can be reached when quantum yields of ISC do not differ much. This is also the case of CQ, where quantum yield of ISC is near to 1 [3,14].

3.4. Mechanism of photo-conversion of CQ

The mechanism proposed for CQ photo-oxidation in liquid solutions (Scheme 1) [17–19] is probably operative in the polymer films, also. Addition of molecular oxygen to CQ affords the peroxy–alkoxy biradical intermediate **10**, which can then form the cyclic camphordiacyl peroxide (**12**) either directly or via the dioxetane (**11**). In polymer matrices with easily abstractable H-atoms, like PS, **12** is the probable precursor of camphoric diacid (**7**). Its formation may also lead to some cleavage of PS chains. Alternatively, **10** may form camphoric anhydride (**6**) by loosing an oxygen atom



Scheme 1.



Scheme 2.

to another molecule of CQ, to another molecule of oxygen (forming ozone), or to the polymer [17–19].

CQ appears to react in polymer films via two competitive pathways whose relative importance depend on the local concentration of molecular oxygen and the availability of easily abstractable H-atoms. Triplet states of CQ are the main reactants with molecular oxygen to yield camphoric acid and camphoric anhydride (Scheme 1 and Eqs. (1) and (2) of Scheme 2). As shown in Eq. (3), the triplet state of CQ can also be quenched by oxygen [16]. However, physical quenching by molecular oxygen must be less efficient than its chemical reaction with CQ because the rate of photo-oxidation increases with molecular oxygen concentration. In addition, efficient reaction of CQ excited states with molecular oxygen precludes alternative pathways involving H-abstraction from polymer chains, which is the process with smaller rate constant (Eq. (4)). Thus the degree, to which a polymer reacts via chain scission [20] by CQ, depends on molecular oxygen concentration too. The CQH$^\bullet$ radical can either abstract another H-atom from a vicinal site (introducing a double bond along the chain) or combine with a chain radical center (Eq. (5)). The MS data demonstrate that the latter does occur to a significant extent in the absence of molecular oxygen. These adducts are analogous to products **1** and **2** obtained upon irradiation of CQ in toluene or *p*-xylene in nitrogen atmospheres.

The rate of CQ consumption in air depends, in the specific conditions, on the type of polymer matrix. It is caused by various oxygen concentrations in the air-equilibrated polymer matrices, coefficients of oxygen diffusion in polymer film and by various stabilization of CQ excited state by polymer matrix. All these factors can influence the rate of CQ consumption.

4. Conclusions

In contrast to benzil [8,9], CQ does not yield a stable intramolecular peroxy anhydride when irradiated in aerated glassy polymer matrices. Only products of its decomposition or related to its proposed precursor **10** could be identified. In the absence of molecular oxygen excited states of CQ abstract H-atoms from and degrade their polymer hosts.

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