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Cationic photopolymerization under visible laser light: polymerization of oxiranes with coumarin/onium salt initiator systems

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The cationic bulk polymerization of oxiranes such as cyclohexene oxide and 4-vinyl cyclohexene dioxide can be induced by light in the visible wavelength range with the aid of an initiator system consisting of an onium salt and a coumarin (appropriate for applications of lasers emitting light between 400 and 500 nm). This was demonstrated by irradiating neat monomers containing either coumarin 153 (C-153) or coumarin 7 (C-7) and isoquinolinium hexafluorophosphate, diphenyliodonium hexafluorophosphate or triphenylsulfonium hexafluorophosphate with a continuous laser beam ($\lambda_{\text{inc}} = 488$ nm). The monomer conversion was limited to ca. 60% due to consumption of the coumarin and insolubility of the onium salt in the polymerizing medium at lower monomer content levels. Initiator fragments were not incorporated into the polymer. In the presence of onium salts, the photolysis of coumarins in the absence of O_2 results in proton formation: $\phi(H^+) = 1.3 \times 10^{-2}$ (C-7) and $\phi(H^+) = 2.3 \times 10^{-2}$ (C-153) and it is concluded that protons play a major role in the initiation of the polymerization. Copyright © 1996 Elsevier Science Ltd.

(Keywords: photopolymerization; oxiranes; coumarin/onium salt initiators)

INTRODUCTION

Recently, the interest in photoinitiator systems applicable to the initiation of free-radical polymerizations under visible light has been revived[1–7]. This revival is caused by the fact that lasers emitting light at $\lambda > 400$ nm have become commercially available and applications of laser-induced polymerizations for various modern technologies such as three-dimensional machining, photoimaging, holography or microlithography, have become feasible. Under these aspects, visible light-induced cationic polymerizations are also interesting, because of the large variety of readily available monomers which are cationically but not radically polymerizable, such as oxiranes or vinyl ethers. During the last few years our efforts have concerned ultra-violet (u.v.) light-induced polymerizations of such monomers[8–10] and, quite recently, we have also started to investigate cationic polymerizations induced by lasers emitting visible light. In this connection, it is interesting to refer to the earlier work of Crivello and Lam[11] who studied the *dye-sensitized* photolysis of iodonium salts and the cationic polymerization of some oxiranes initiated by this means. Our recent work, which is dealt with in this paper concerns the laser light-induced cationic polymerization of several oxiranes by the aid of coumarins. It was found that cyclohexene oxide (CHO), and 4-vinyl cyclohexene dioxide (4VCHD), can be readily polymerized in bulk at room temperature upon irradiation with 488 nm laser light emitted by an argon ion laser. The initiator systems employed consisted of a coumarin (number 7 or 153) and an onium salt such as *N*-ethoxy-isoquinolinium hexafluorophosphate ($EIQ^+PF_6^-$), diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$), or triphenylsulfonium hexafluorophosphate ($Ph_3S^+PF_6^-$).

To our knowledge coumarins have not yet been examined regarding their capability to act as photoinitiators for cationic polymerization.

EXPERIMENTAL

Materials

3-(2′-Benzimidazolyl)-7-*N*,*N*-diethylamino coumarin (coumarin 7 (C-7)), and 9-trifluoromethyl-2,3,6,7-tetrahydro-1*H*, 5*H*-[1]benzopyrano[6,7,8,*i*,*j*]chinolizin-11-one (coumarin 153 (C-153)), were used as received from Aldrich. The salt $EIQ^+PF_6^-$ was prepared according to the method of Reichardt[12] by reacting triethyl oxonium hexafluorophosphate (Aldrich) with isoquinolinium-*N*-oxide (Aldrich), as described previously[10]. The salt $Ph_2I^+PF_6^-$ was prepared as described in the literature[13]. 2,6-Di-tert-butyl-4-methylpyridine (DBMP), obtained from Aldrich, was used as received. (±)-1,2-Propylene carbonate ((±)-4-methyl-1,3-dioxolan-2-one), was purchased from Aldrich. Cyclohexene oxide (CHO) (7-oxabicyclo[4.1.0]heptane), obtained from Aldrich, and 1,4-butanediol-diglycidyl ether (BGE) obtained from Ciba-Geigy, were refluxed over $CaCl_2$ for several hours and then fractionally distilled. 4-Vinyl cyclohexene dioxide (4VCHD, Fluka) was fractionally distilled (b.p. 87–88°C at 4 torr).

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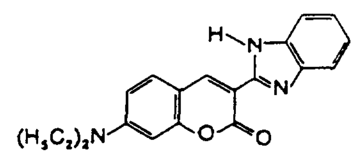
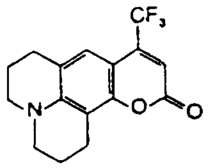
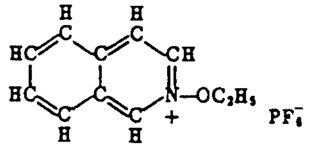


Coumarin 7



Coumarin 153



EIQ⁺PF₆⁻

Irradiations

Appropriate amounts of the initiator compounds were dissolved in the monomer and 0.3 ml samples contained in test tubes were irradiated at $\lambda_{inc} = 488$ nm under argon, oxygen or air. Most irradiations were conducted with a continuously emitting ion laser (Spectraphysics, laser power = 0.5 W). Irradiations at various intensities were performed by inserting appropriate filters in the laser beam. Moreover, for low-intensity irradiations a xenon lamp (Osram XBO, 450 W), operated in conjunction with a monochromator set at 488 nm, was used. Actinometry was performed with the aid of the potassium ferrioxalate actinometer ($\phi(Fe^{2+}) = 0.9$).

Determination of monomer conversion and characterization of polymers

The bulk polymerization was monitored in the case of 4VCHD by determining gravimetrically the amount of polymer formed, and in the case of CHO by determining the monomer conversion with the aid of size exclusion chromatography using a set of Ultrastyragel columns (Waters, 500, 10^3, 10^4 and 10^5 Å) with tetrahydrofuran as eluent. The molar mass of the poly(cyclohexene oxide) samples was estimated from the size exclusion chromatograms on the basis of a calibration curve obtained with polystyrene standards.

Determination of proton concentrations

Coumarin 153 was irradiated, at a concentration of 3.2×10^{-4} mol dm^{-3}, in argon- or oxygen-saturated propylene carbonate solution containing $EIQ^+PF_6^-$ (1.3×10^{-2} mol dm^{-3}). Water and methanol were added to the irradiated solution at a volume ratio of 1.0 : 2.0 : 0.4 (irradiated solution : water : methanol). Subsequently, the proton concentration was measured with a glass electrode (Ingold 405-S7) which was calibrated with the aid of a standard HCl solution. Analogous experiments were performed with coumarin 7.

RESULTS

Optical absorption spectra

Figure 1 shows the optical absorption spectra of C-153 and C-7 recorded in CHO solutions in the absence of onium salts. The maxima of the broad bands of the spectra at ca. 415 and 435 nm, respectively, are attributed to $\pi \rightarrow \pi^*$ transitions[14]. The intensity and shape of these bands were not altered by the addition of $Ph_2I^+PF_6^-$ or $EIQ^+PF_6^-$, thus indicating that there is no ground state interaction between coumarins and onium ions. Actually, the extinction coefficients (at 488 nm) of the coumarins, dissolved in the monomers used in the polymerization studies, are not equal. Therefore, coumarin concentrations were chosen so that in all cases ca. 25–35% of the incident light was absorbed by the sample.

Polymerization experiments with CHO

Argon-saturated CHO containing only coumarin 7 or 153, or only $EIQ^+PF_6^-$ or $Ph_2I^+PF_6^-$ did not polymerize upon irradiation at $\lambda_{inc} = 488$ nm. However, argon-saturated CHO containing both a coumarin and $Ph_2I^+PF_6^-$ or $EIQ^+PF_6^-$ polymerized readily upon irradiation at $\lambda_{inc} = 488$ nm at room temperature. It is noticeable that $Ph_3S^+PF_6^-$ in conjunction with C-153 is also capable of acting as a photoinitiator for the polymerization of CHO, although only a few preliminary experiments have been performed so far with this initiator couple. From *Figures 2a* and *b*, where typical conversion–time profiles are shown, it can be seen that the curves bend over towards the abscissa after an initial linear increase and then approach a limiting value which is definitely lower than 100%. Notably, onium salt crystals precipitated as the monomer conversion increased. This explains to some extent why the monomer conversion approaches a limiting value. Other factors contributing to this effect are the consumption of coumarin in the early stages of irradiation and the formation of reaction products which absorb rather strongly at $\lambda_{inc} = 488$ nm (see below). Interestingly, the polymerization of CHO continued slowly after the irradiation was stopped, as can be seen from *Figure 3*.

Molecular oxygen significantly retards the polymerization of CHO. As can be seen from *Table 1* the limiting conversion becomes lower when the system contains molecular oxygen. This effect is less pronounced in the case of C-7 than in the case of C-153. Since O_2 does not react with the growing chains of poly(cyclohexene oxide) it must affect the formation of the initiating species (see below). Tributylamine is supposed to react with both the initiating species and the growing chains. It retarded and,

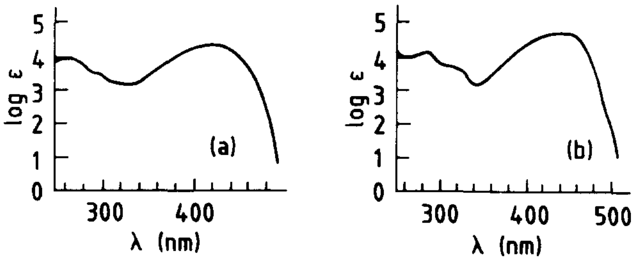


Figure 1 Optical absorption spectra of the coumarins in CHO solution (2×10^{-3} mol dm^{-3}): (a) C-153; (b) C-7. Units used for the extinction coefficient ε are dm^3 mol^{-1} cm^{-1}

at rather high concentrations (0.137 mol dm^{-3}), inhibited the polymerization of CHO completely. Interestingly, the polymerization of CHO is also retarded by the hindered pyridine DBMP which is frequently used as a proton scavenger. Typically a four fold decrease in the rate of monomer conversion was measured when argon-saturated CHO containing coumarin 153 (3.4× 10^{-3} mol dm^{-3}), EIQ$^+$PF$_6^-$ (0.11 mol dm^{-3}), and DBMP (1.1 × 10^{-2} mol dm^{-3}) was irradiated at 488 nm. In this connection, it is noticeable that an argon-saturated propylene carbonate solution, containing coumarin 153 (3.2 × 10^{-4} mol dm^{-3}) and EIQ$^+$PF$_6^-$ (1.3× 10^{-2} mol dm^{-3}), but no CHO, irradiated at 488 nm for 1–3 min, initiated the polymerization of CHO when it was mixed with the latter in a 1 : 1 ratio. From this result it was concluded that the photolysis of C-153 results in stable products, probably protons, which are capable of initiating the polymerization of CHO.

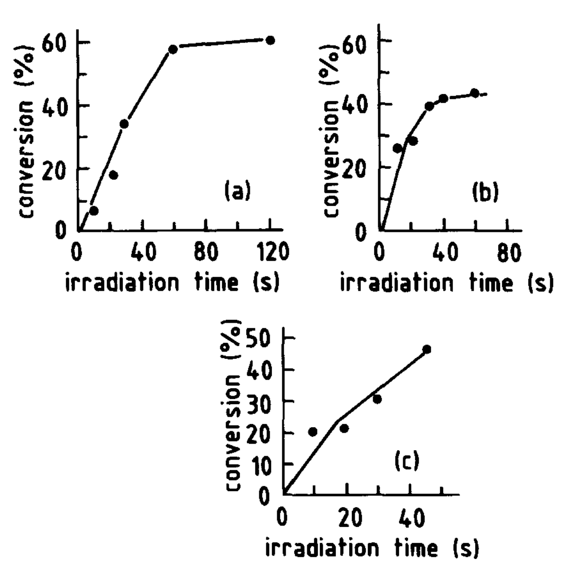


Figure 2 Bulk polymerization under Ar of CHO (a) and (b), and of 4VCHD (c), at λ_{inc} = 488 nm, DR_{abs} = -6 × 10^{-2} einstein dm^{-3} min^{-1} and T = 23°C. Monomer conversion as a function of the irradiation time. Initiator system: (a) C-153 (3.4 × 10^{-3} mol dm^{-3}), EIQ$^+$PF$_6^-$ (0.11 mol dm^{-3}); (b) C-7 (1.2 × 10^{-3} mol dm^{-3}), EIQ$^+$PF$_6^-$ (0.11 mol dm^{-3}); (c) C-153 (8.0 × 10^{-4} mol dm^{-3}), EIQ$^+$PF$_6^-$ (0.10 mol dm^{-3})

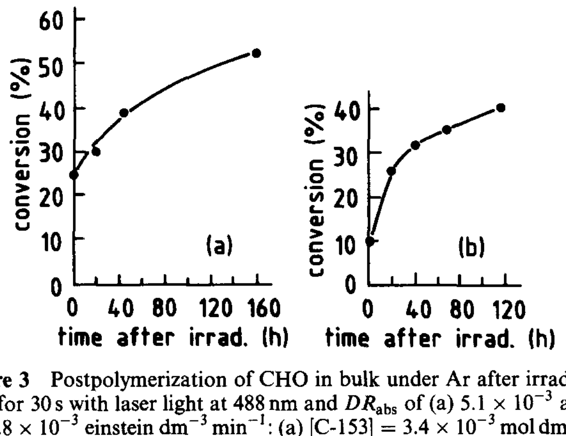


Figure 3 Postpolymerization of CHO in bulk under Ar after irradiation for 30 s with laser light at 488 nm and DR_{abs} of (a) 5.1 × 10^{-3} and (b) 7.8 × 10^{-3} einstein dm^{-3} min^{-1}: (a) [C-153] = 3.4 × 10^{-3} mol dm^{-3}, [EIQ$^+$PF$_6^-$] = 0.11 mol dm^{-3}; (b) [C-7] = 4.8 × 10^{-4} mol dm^{-3}, [EIQ$^+$PF$_6^-$] = 0.11 mol dm^{-3}

The intensity dependence of the rate of polymerization v_p was studied with the system C-153/EIQ$^+$PF$_6^-$. The v_p values obtained from the initial linear portion of the conversion versus time curves are plotted in *Figure 4* as a function of the absorbed dose rate, DR_{abs}; v_p is directly proportional to the absorbed dose rate, i.e $v_p \propto (DR_{abs})^{\alpha}$, where $\alpha = 1.0$.

The average degree of polymerization of the polymers as estimated from size exclusion chromatography is ca. 250. By recording the optical absorption spectra of the polymers after several reprecipitations from dichloromethane solution with methanol it became evident that initiator fragments are not chemically incorporated into the polymer. The spectra resemble closely the spectrum of PCHO that has been polymerized with the aid of triethyloxonium ions under dark conditions.

Polymerization experiments with other oxiranes

Other oxiranes containing the initiator systems C-153/EIQ$^+$PF$_6^-$ or C-7/EIQ$^+$PF$_6^-$ polymerized readily upon irradiation with laser light at λ_{inc} = 488 nm. Insoluble gels were formed when the bifunctional monomers 4VCHD and BGE were irradiated. A typical plot depicting the conversion of 4VCHD as a function of the irradiation time is shown in *Figure 2c*. The conversion–time profiles resemble those obtained with CHO, i.e. the conversion always approaches a limiting value which is appreciably lower than 100%. Oxygen also exerts an inhibitive effect on the polymerization of 4VCHD and BGE. Again, the initiator action of C-153 is more strongly affected by O$_2$ than that of C-7. For example, 4VCHD did not gel upon irradiation under O$_2$, i.e. the monomer did not polymerize when it contained

Table 1 Bulk polymerization of CHO under argon at T = 23°C and DR_{abs} = 6.14 × 10^{-2} einstein dm^{-3} min^{-1} [a]

	Monomer conversion[b]		
Atmosphere	Initiator system C-153/EIQ$^+$PF$_6^-$	Initiator system C-7/EIQ$^+$PF$_6^-$	Initiator system C-153/Ph$_2$I$^+$PF$_6^-$
O$_2$	18	11	35
Air	50	–	–
Ar	60	24	56

[a] [C-153] = 3.4 × 10^{-3} mol dm^{-3}; [C-7] = 4 × 10^{-4} mol dm^{-3}; [EIQ$^+$PF$_6^-$], [Ph$_2$I$^+$PF$_6^-$] = 0.11 mol dm^{-3}
[b] Monomer conversion after 3 min irradiation

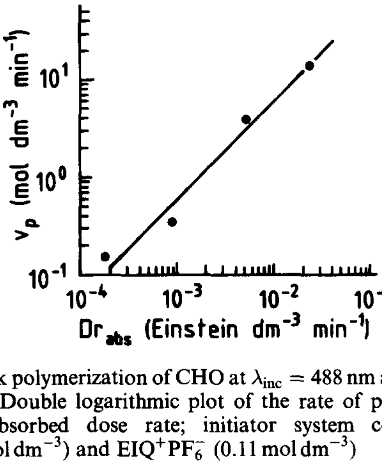


Figure 4 Bulk polymerization of CHO at λ_{inc} = 488 nm and T = 23°C under argon. Double logarithmic plot of the rate of polymerization *versus* the absorbed dose rate; initiator system coumarin 153 (2.5 × 10^{-3} mol dm^{-3}) and EIQ$^+$PF$_6^-$ (0.11 mol dm^{-3})

the initiator system C-153/$EIQ^+PF_6^-$. However, a gel was formed, but at a reduced rate, in the presence of O_2 when C-153 was replaced by C-7. DBMP (0.01 mol dm^{-3}) also acted as a polymerization retarder in these cases.

Photochemical reactions of coumarins 7 and 153

Photodecomposition of the coumarins. Both coumarins were not converted upon irradiation of both aerated and argon-saturated CHO solutions in the absence of an onium salt at $\lambda_{inc} = 488$ nm. This was inferred from the fact that the optical absorption spectra were not altered during irradiation. However, in the presence of $EIQ^+PF_6^-$, $Ph_2I^+PF_6^-$, or $Ph_3S^+PF_6^-$, both coumarins readily decomposed upon irradiation at 488 nm. Notably, at this wavelength the onium salts are completely transparent. Typical results demonstrating the photodecomposition of C-153 are presented in *Figure 5a*. It can be seen that apart from the coumarin band at around 415 nm, which steadily decreased with increasing irradiation time, the band due to EIQ^+ ions at 325 nm also underwent significant changes. It increased strongly at first, indicating the formation of light-absorbing reaction products, and then later decreased. Notably, the reaction products also absorb light at wavelengths exceeding the range of the initial absorption spectrum of the reaction mixture, as can be seen from *Figure 5b*. The inset in the latter figure shows how the absorption at $\lambda = 480$ nm increased as the result of the formation of a new product. Thus, it becomes obvious that electronically excited C-153 reacts effectively with EIQ^+ ions, with excited C-7 exhibiting a similar behaviour.

Detection of protons. On the basis of the results obtained concerning the polymerization of CHO and other oxiranes it was conjectured that protons are formed upon the photolysis of both C-7 and C-153 in the presence of onium salts. Actually, protons were detected by potentiometric measurements with the aid of a glass electrode when propylene carbonate solutions containing $EIQ^+PF_6^-$ (1.3×10^{-2} mol dm^{-3}) and C-7 (1.5×10^{-4} mol dm^{-3}) or C-153 (3.2×10^{-4} mol dm^{-3}) were irradiated at $\lambda_{inc} = 488$ nm. *Figure 6* shows plots of the proton concentration *versus* the absorbed dose. From the slopes of the straight lines, quantum yields $\phi(H^+)$ for the formation of protons were obtained. Interestingly, oxygen did not influence proton formation in the case of C-7, where $\phi(H^+) = 1.3 \times 10^{-2}$ was found both in the presence and absence of oxygen. By contrast, in the case of C-153, oxygen significantly retarded proton formation, i.e. $\phi(H^+) = 2.3 \times 10^{-2}$ (O_2 absent) and $\phi(H^+) = 1.2 \times 10^{-3}$ (O_2 present).

Luminescence quenching. Fluorescence studies with C-7 and C-153 in CH_2Cl_2 solution at $\lambda_{exc} = 435$ and 450 nm, respectively, revealed the following: $EMP^+PF_6^-$, $EIQ^+PF_6^-$ and $Ph_2I^+PF_6^-$ quench the strong fluorescence of both coumarins. Notably, the emission of C-7 was quenched more effectively than that of C-153. However, quantitative data were accessible only in the case of C-153. In the case of C-7 the decay of the emission spectrum was accompanied by the formation of a new less intensive spectrum with a maximum shifted to longer wavelengths. Stern–Volmer constants are compiled in *Table 2*, which also contains values obtained for the quenching rate constant k_q calculated with the aid of $k = 1.8 \times 10^8\ s^{-1}$, i.e. the decay rate constant of excited singlets, as reported by Jones *et al.*[15]. With respect to the order of magnitude of k_q it is concluded that the onium compounds under investigation here undergo encounter-controlled reactions with excited C-153 and C-7. Interestingly, oxygen (at 10^5 Pa) quenched the fluorescence of C-153 but did not quench the fluorescence of C-7, which is in accord with the singlet lifetime of C-7 being significantly shorter than that of C-153[15].

Table 2 Quenching of the fluorescence of C-153

Quencher	K_{SV}[a] ($dm^3\ mol^{-1}$)	$k_q \times 10^{10}$[b] ($dm^3\ mol^{-1}\ s^{-1}$)
$EMP^+PF_6^-$[c]	200	3.6
$EIQ^+PF_6^-$	170	3.1
$Ph_2I^+PF_6^-$	65	1.2

[a] $K_{SV} = k_q/k$, measured in CH_2Cl_2 solution at 23°C, with $\lambda_{exc} = 450$ and $\lambda_{obs} = 500$ nm

[b] Calculated using $k = 1.8 \times 10^8\ s^{-1}$ (ref. 15)

[c] EMP^+ = *N*-ethoxy-2-methyl pyridinium

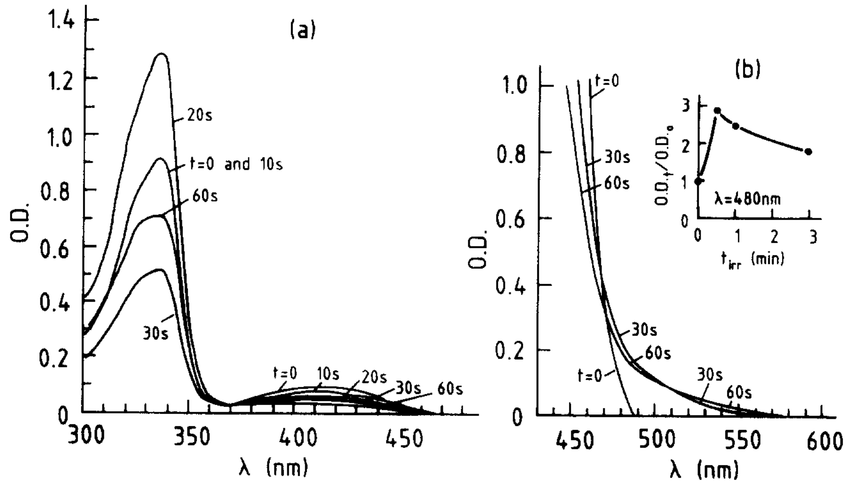


Figure 5 Optical absorption spectra of CHO solutions containing $EIQ^+PF_6^-$ (0.11 mol dm^{-3}) and C-153 (3.4×10^{-3} mol dm^{-3}) recorded before and after irradiation at $\lambda_{inc} = 488$ nm under argon at $T = 23$°C. Prior to recording, the solutions were diluted with THF (1/100, vol/vol) (a) or with CH_2Cl_2 (1/1 vol/vol) (b). The inset in *Figure 4b* presents the change in the optical density at 480 nm as a function of the irradiation time

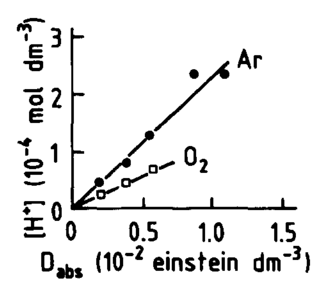


Figure 6 Proton formation in propylene carbonate solution containing C-153 ($3.4 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$) and $\mathrm{EIQ^+PF_6^-}$ ($1.3 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$). Plot of the proton concentration of the irradiated solution *versus* the absorbed dose; $\lambda_{\mathrm{inc}} = 488$ nm, absorbed dose rate $= 5.7 \times 10^{-3}$ einstein $\mathrm{dm^{-3}\,min^{-1}}$

DISCUSSION

The results presented in this paper show that when used in conjunction with the isoquinolinium salt $\mathrm{EIQ^+PF_6^-}$, the iodonium salt $\mathrm{Ph_2I^+PF_6^-}$ or the sulfonium salt $\mathrm{Ph_3S^+PF_6^-}$, coumarin 7 and coumarin 153 are both capable of initiating the cationic photopolymerization of oxiranes. This was demonstrated in the case of the monofunctional monomer CHO and of two bifunctional monomers. In all cases the monomer conversion was limited to a maximum of ca. 60%. This is due to the rapid photodecomposition of the coumarin and the fact that monomer conversion rendered the onium salts insoluble in the polymerizing system, thus causing their precipitation. Attempts to elucidate the mechanism of the initiation process revealed that photogenerated protons play a major role in initiating the cationic polymerization. A pronounced postpolymerization, which was typical for cationic polymerization of oxirane compounds, was also observed in this work with CHO. This is very likely to be due to the action of a protic acid which is generated during the irradiation. The acid dissociates steadily at a low rate, as protons are consumed by reaction with the monomer. From the fact that both coumarins are photostable at $\lambda_{\mathrm{inc}} = 488$ nm, but are photodecomposed in the presence of onium salts, it is concluded that excited coumarin molecules react with onium ions. For many coumarins, including C-7 and C-153, it has been reported[14] that the quantum yield for intersystem crossing is negligibly low, which implies that deactivation and chemical reactions occur essentially from the singlet manifold. Singlet lifetimes of a few ns (ca. 5 ns in the case of C-153), which are hardly affected by the polarity of the medium, have been determined by fluorescence measurements[15]. *Scheme 1* describes the excitation, and the deactivation routes, including the reaction with onium ions ($\mathrm{On^+}$) and $\mathrm{O_2}$.

The rather fast decay of excited singlets according to reactions (2a) and (2b) affords a rather higher onium salt concentration in order to guarantee a high conversion of coumarin according to reaction (3). For instance, on the basis of $k = 1.8 \times 10^{8}\,\mathrm{s^{-1}}$ and $k_q = 4 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}}$, the occurrence of reaction (3) with a probability of 95% affords an onium salt concentration of $0.1\,\mathrm{mol\,dm^{-3}}$. Regarding the nature of reaction (3), energy transfer can be excluded for energetic reasons and electron transfer from $^1\mathrm{Cou}^*$ to an onium ion is very likely to occur. This is substantiated to some extent by the high bimolecular rate constant, of the order of $10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, estimated for C-153 (see *Table 2*). The pronounced retardation of the rate of polymerization by oxygen, observed with systems containing C-153, indicates that the oxygen strongly competes with the onium ions for the reaction with singlet excited coumarin molecules according to reactions (3) and (4). However, because of the rather short singlet lifetime of C-7, reaction (3) is scarcely affected by $\mathrm{O_2}$ (at 10^5 Pa) in this case. Therefore, C-7 is a compound more appropriate for the initiation of cationic polymerizations under air than C-153.

$$ {}^1\mathrm{Cou} \xrightarrow{h\nu} {}^1\mathrm{Cou}^* \qquad (1) $$

$$ {}^1\mathrm{Cou}^* \xrightarrow{k_1} \begin{cases} {}^1\mathrm{Cou} + \; h\nu \text{ (emission)} \\ {}^1\mathrm{Cou} + \; \Delta \text{ (collisional deactivation)} \end{cases} $$

$$ {}^1\mathrm{Cou}^* + \mathrm{On}^* \xrightarrow{kq} \text{Products} \qquad (3) $$

$$ {}^1\mathrm{Cou}^* + \mathrm{O_2} \xrightarrow{k_2(\mathrm{O_2})} {}^1\mathrm{Cou} + \mathrm{O_2}^* \qquad (4) $$

Scheme 1 Deactivation routes of singlet excited coumarin (^{1}Cou*)

The elaboration of further details of the mechanism affords much additional research, and in particular more work concerning the analysis of the photoproducts.

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