

# Visible Laser Lights in Photoinduced Polymerization.

## VI. Thioxanthenes and Ketocoumarins as Photoinitiators

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### SYNOPSIS

The efficiency of thioxanthenes and ketocoumarins as photoinitiators has been checked in visible laser light-induced polymerization reactions and discussed in terms of excited-state reactivity (as revealed by time-resolved laser spectroscopy). These compounds undergo fast electron transfer reactions in the presence of amines and onium salts. Transient absorption spectra and rate constants of the processes involved have been determined. The combination photoinitiator-amine-onium salt appears as very promising for the design of efficient photosensitive systems.

### I. INTRODUCTION

The fast development during the last decade of high-performance UV-curable systems has induced a growing number of applications in various industrial areas.<sup>1</sup> For some specific applications such as photoimaging or microelectronics, lasers can replace the conventional mercury lamps as a high-intensity light source to produce initiating radical or cationic species to start the chain polymerization reaction; in holography, laser sources must be necessarily used.<sup>2</sup> With regard to the initiation step, the main problem is to define photosensitive systems (PSSs), whose absorption spectra match the laser emission wavelength. In the UV part of the spectrum, this is readily achieved by using photoinitiators.<sup>3,4</sup> Photoinitiation under visible lights is induced through two different processes:

- Direct absorption of light by PSSs. In that case, the PSS plays the role of a photoinitiator: Examples are known in dyes<sup>5</sup> and in substituted usual UV compounds (in which an appropriate

substitution leads to a red shift of the absorption).

- Sensitized formation of initiating systems. The PSS should contain a photosensitizer and a photoinitiator (the former absorbs the light and then transfers its excitation to the latter).

In both cases, the reactivity in the excited states will govern the efficiency of the PSSs. In the present paper, the primary processes involved after light absorption will be investigated in two classes of compounds: thioxanthenes (TX) and ketocoumarins (KC). These compounds are sensitive under laser beams: For example, for TX and KC, the Ar<sup>+</sup> laser (363.8 nm) and the HeCd laser (441.6 nm), and for KC, the Ar<sup>+</sup> laser (488, 514 nm),<sup>6</sup> have been shown as efficient photoinitiators<sup>7-9</sup> or photosensitizers of the cross-linking reaction<sup>10</sup> and polymerization of pigmented media.<sup>11</sup>

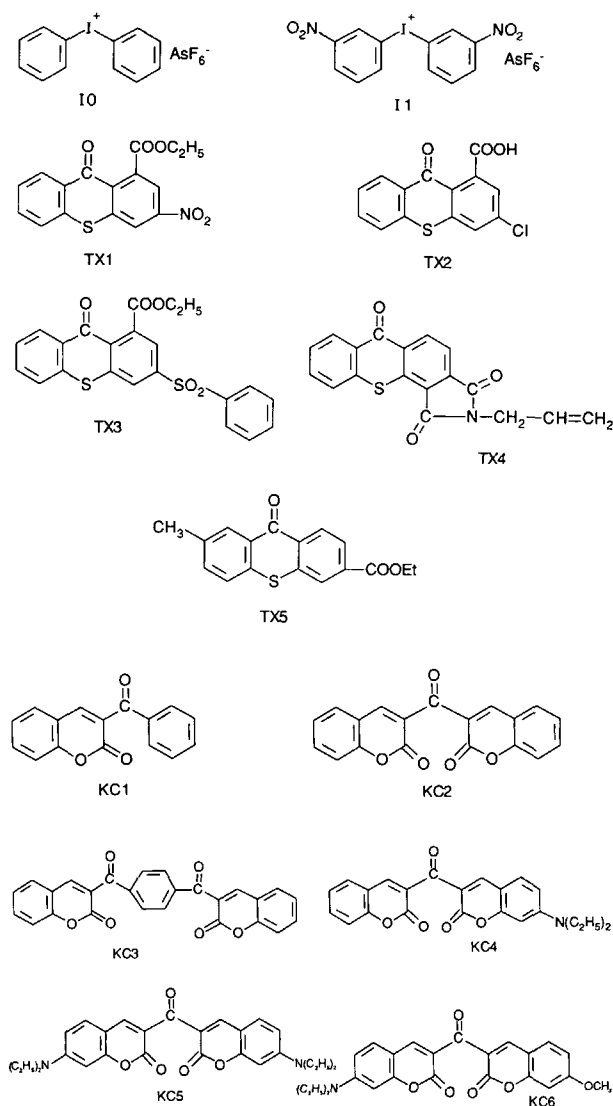
### II. EXPERIMENTAL

#### 1. Materials

The following compounds have been used: I0 and I1 were obtained from Crivello,<sup>12</sup> TX1-TX5 were from Drs. Rutsch and Dietliker (Ciba Geigy, Fribourg), and KC1-KC3 were prepared as reported in Ref. 6 or Ref. 13 according to a previous work of Eastman Kodak<sup>14</sup>:

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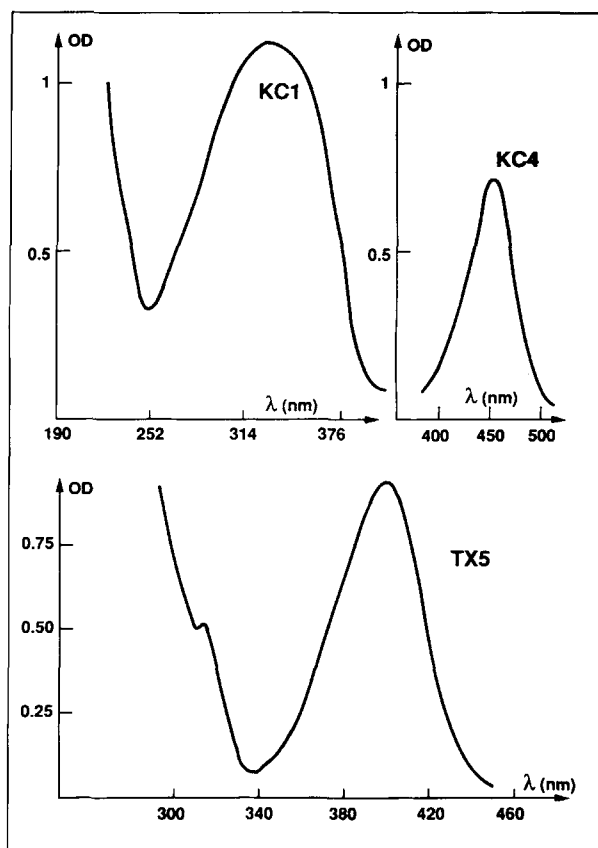
Representative ground-state absorptions in the UV and near-UV are shown in Figure 1.

The monomers used are methyl methacrylate (MMA), pentaerythritol triacrylate (PETA), trimethylpropane acrylate (TMPTA), and an epoxy acrylate E605 from UCB.

## 2. Techniques

Solution photopolymerization experiments have been carried out under exposure to an HPK 125 W lamp, either at  $\lambda = 365$  nm or  $\lambda \geq 400$  nm, in degassed solution. The % conversion is determined gravimetrically.

In film experiments, the photopolymerizable system is exposed either to a 80 W  $\text{cm}^{-1}$  mercury lamp or laser lights (continuous Ar<sup>+</sup> laser at  $\lambda = 363.8$  or 488 nm or a pulsed Nd/YAG laser pumped dye laser



**Figure 1** UV-absorption spectra of KC1, KC4, and TX5 in acetonitrile.

operating at  $\lambda = 440$  nm). The energy dose  $D$  necessary to have a tack-free coating is defined by

$$D = I_0(1 - e^{-2.30D})t$$

where  $I_0$ ,  $OD$ , and  $t$  are the intensity of the light beam ( $\text{phot cm}^{-2} \text{ s}^{-1}$ ), the optical density of the sample at the excitation wavelength, and the exposure time, respectively.

The time-resolved laser-spectroscopy apparatus has been fully described<sup>8</sup>: The excitation consists in a 3 ns pulse at  $\lambda = 355$  nm. The time resolution of the analyzing device is 3 ns.

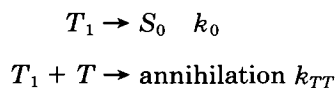
## III. RESULTS

### 1. Excited-State Processes

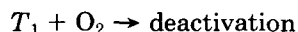
#### A. The Triplet State

Laser flash experiments were carried out to induce the  $S_0$ - $S_1$  transition of TXs and KCs. Short singlet-state  $S_1$  lifetimes are associated with low fluores-

cence intensity even in methanol, e.g., 4.4, 1.0, and 2.5 ns for TX2, TX3, and TX4, respectively. This  $S_0$ - $S_1$  transition is followed by a fast intersystem crossing  $S_1$ - $T_1$ , leading to long-lived triplet states (in the  $\mu$ s time range) that decay according to first-order and second-order kinetics in deaerated toluene or acetonitrile solutions:

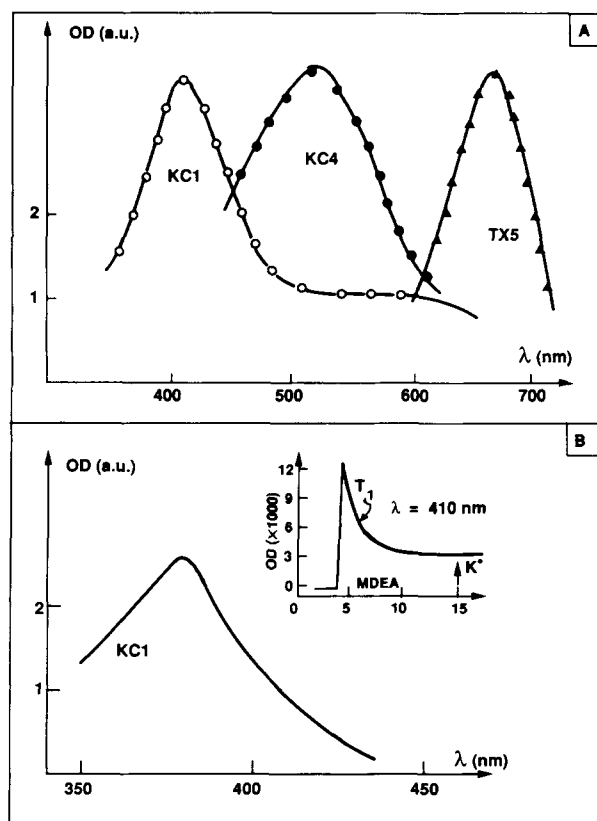


In aerated solutions, the decay is first order:



The rate constant of this reaction  $k_q^{O_2}$  is calculated from the triplet-state lifetime  $\tau_T$ :  $\tau_T^{-1} = k_q^{O_2} [O_2]$ . Typical values are ranging from 1 to 2.5  $\times 10^9 M^{-1} s^{-1}$ .

The transient triplet-triplet absorption resulting from excitation of TXs and KCs were monitored



**Figure 2** Transient absorption spectra of KC1: triplet state (A) and ketyl radical (B); KC4: triplet state (A); TX5: triplet state (A). Solvent: toluene.

**Table I** Rate Constant of Quenching by Amines  $k_e$

	MDEA	TEA
	[ $10^{-9} k_e (M^{-1} s^{-1})$ ]	
KC1	2.5 <sup>a</sup>	3.6 <sup>a</sup>
KC2	1.5	3.6
KC3	3.2	4.8
KC4	0.05 <sup>b</sup>	
KC5	0.03	
TX1	10 <sup>b</sup>	
TX2	2.6	
TX3	3.4	
TX4	4.0	
TX5	3	

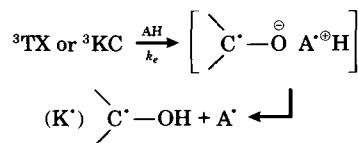
<sup>a</sup> In acetonitrile.

<sup>b</sup> In toluene.

between 350 and 700 nm. Such absorptions are shown in Figure 2.

### B. Quenching by Amines

In the presence of amines (AH) such as methyldiethanolamine (MDEA), TXs and KCs undergo a fast electron transfer process followed by a proton transfer process that results in the generation of a ketyl-type radical  $K'$ . The transient absorption spectrum of  $K'$  is displayed in Figure 2:



The rate constant of the bimolecular interaction between the ketone and the amine is calculated from the usual Stern Volmer plot of the triplet state lifetime  $\tau_T$  as a function of the amine concentration  $[\text{AH}]$ :

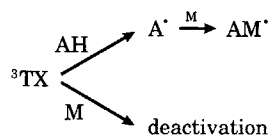
$$\frac{1}{\tau_T} = k_0 + k_e[\text{AH}]$$

The results are included in Table I: The  $k_e$  values (except that for KC4) correspond to that usually reported for the amine quenching of ketone triplet states.

### C. Quenching by Monomers

It is a well-known fact that monomer (M) quenching of triplet states is a detrimental pathway that com-

petes with the generation of the active species (ionic or radical) being able to start the polymerization reaction, e.g.:



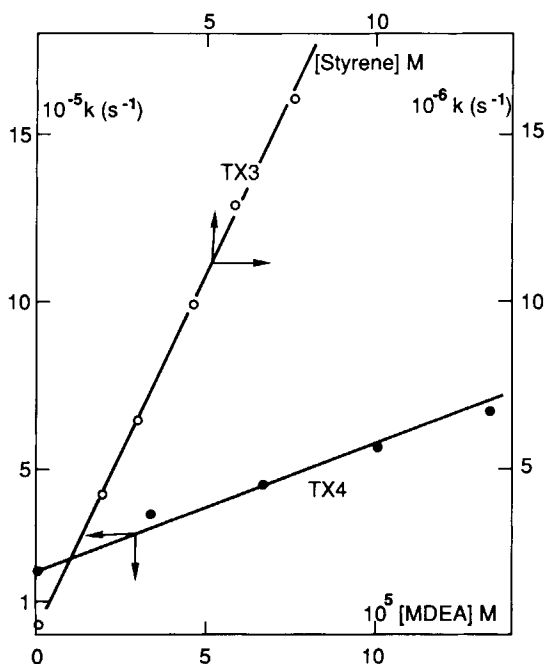
Rate constants  $k_q$  of this reaction are evaluated from the slope of the Stern Volmer plot (Fig. 3):

$$\frac{1}{\tau_T} = k_0 + k_q[\text{M}]$$

Table II gives the  $k_q$  values for the quenching of the triplet states by methyl methacrylate (MMA), styrene (ST), and cyclohexenoxide (CHO): These values are rather very low for CHO, low for MMA, and high for ST. Compounds KC4 and TX5 exhibit a specific behavior: The rate constants differ significantly from that of the parent compounds. The trend observed in all these data compares well with the results of quenching in chlorothioxanthone or benzophenone.<sup>15,16</sup>

#### D. Quenching by Iodonium Salts (I)

Electron transfer between triplet states of ketones and onium salts has been shown to occur, e.g., in



**Figure 3** Typical Stern Volmer plot for the triplet-state quenching by amine and monomer.  $k$ : rate constant of disappearance of the triplet ( $k: 1/\tau_T$ ).

**Table II** Rate Constant of Quenching by Monomer  $k_q$

	MMA	ST	CHO
	[ $10^{-6} k_q (\text{M}^{-1} \text{s}^{-1})$ ]		
KC1	11 <sup>a</sup>	850 <sup>a</sup>	4 <sup>a</sup>
KC2	26	950	6
KC3	12	1600	
KC4	0.03 <sup>b</sup>		
TX1	40 <sup>b</sup>	170 <sup>b</sup>	1 <sup>a</sup>
TX2	8	280	
TX3	22	2000	
TX4	7	860	
TX5	0.02		

<sup>a</sup> In acetonitrile.

<sup>b</sup> In toluene.

the system chlorothioxanthone CTX/diphenyliodonium salt<sup>17</sup>: in that case, the ketone plays the role of an electron donor (the cation radical is detected<sup>17</sup> and iodobenzene is formed):

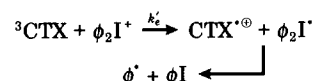


Table III lists the values of  $k'_e$  for the quenching of KCs and TXs by I0 and I1 calculated from (Fig. 4):

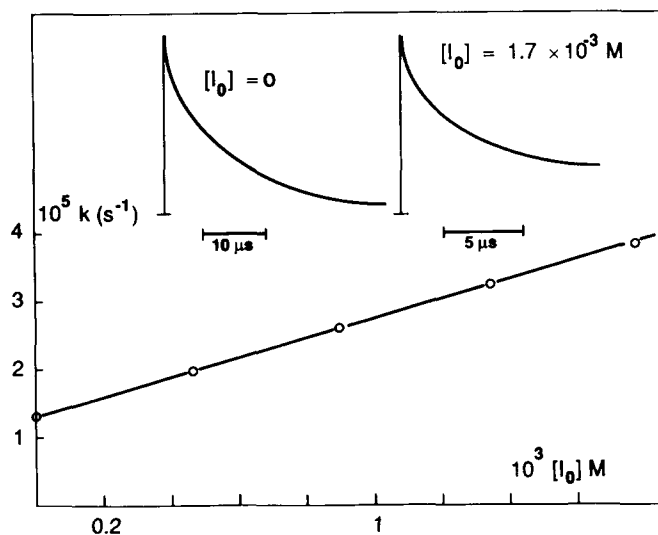
$$\frac{1}{\tau_T} = k_0 + k'_e[\text{I}]$$

**Table III** Rate Constant  $k'_e$  of Quenching by I0 and I1

	I1	I0
	[ $10^{-7} k'_e (\text{M}^{-1} \text{s}^{-1})$ ]	
KC1	310 <sup>a</sup>	6.5 <sup>a</sup>
KC2	270	13
KC3	400	
KC4		250 <sup>b</sup>
KC5		200 <sup>b</sup>
TX1		62 <sup>a</sup>
TX2		19
TX3		46
TX4		14

<sup>a</sup> In acetonitrile.

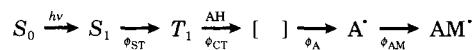
<sup>b</sup> In toluene + 0.7M MeOH.



**Figure 4** Stern Volmer plot for the quenching of the triplet state of KC5 by diphenyl iodonium salt. Typical oscillogram traces at  $\lambda = 420$  nm, in the presence and in the absence of onium salt, showing the decay of the triplet state and the formation of a new long-lived absorbing species ascribed to the cation radical of the ketocoumarin.

### E. Quantum Yield of Electron Transfer

The initiation step of the radical polymerization reaction can be represented by the following sequence of reactions:



The quantum yield of initiation  $\phi_i$  and electron transfer  $\phi'_{CT}$  are expressed by

$$\phi'_{CT} = \phi_{ST}\phi_{CT}$$

$$\phi_i = \phi'_{CT}\phi_A\phi_{AM}$$

with

$$\phi_{CT} = \frac{k_e[AH]}{k_0 + k_q[M] + k_e[AH]}$$

$$R_p = K\sqrt{\phi_i}$$

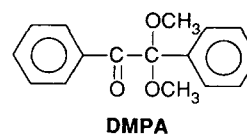
where  $R_p$  is the rate of polymerization.

## 2. Photopolymerization Experiments

Several types of photopolymerization experiments have been carried out to check the ability of TXs and KCs as photoinitiators.

### A. Photopolymerization of MMA in Solution under UV Light

Table IV summarizes the values of  $R_p$ ,  $\phi_i$  (calculated from  $R_p$ ), and  $\phi_{CT}$ . These values can be compared to that obtained in the presence of the well-known photoinitiator DMPA (which works according to an  $\alpha$ -cleavage process):



**Table IV** Rate of Polymerization  $R_p$  of MMA 7M in Toluene in the Presence of 0.05M in MDEA ( $\lambda = 366$  nm)

	$10^5 R_p$ (M s <sup>-1</sup> )	$\phi_i$	$10^2 \phi_{CT}$
KC4	8	3	92
TX1	20	16	64
TX2	16	10	70
TX3	38	58	60
TX4	23	21	80
TX5	20	16	99
DMPA	50	100 <sup>a</sup>	—

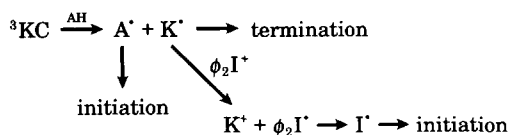
For calculated  $\phi_i$  and  $\phi_{CT}$ , see text.

<sup>a</sup> All  $\phi_i$  values are relative to this reference.

Very high  $\phi_{CT}$ 's are attained, but  $\phi_i$ 's remain lower than that of DMPA. The reason for this should be transferred into a low efficiency of the subsequent reactions occurring after the electron transfer step.

### B. Photopolymerization of MMA in Solution under Visible Light

The experiment has been conducted at  $\lambda \geq 400$  nm. Typical values of  $R_p$  are presented in Table V, which shows that a ketocoumarin is better than eosin. Addition of diphenyliodonium salt to a mixture eosin/amine leads to a two-fold increase of  $R_p$ ; the same holds true in the case of eosin: This behavior has been recently discussed<sup>18</sup> in eosin/onium salt/MDEA in terms of an effect of the salt in the termination reactions. In the case of KC, a plausible mechanism involves the quenching of the ketyl-type radical by the iodonium salt; in fact, this type of radical structure is known to terminate the growing of the polymer chains<sup>19</sup>:



Because of the values of  $k_e$  and  $k'_e$  (Table I), quenching of  ${}^3\text{KC}$ , e.g., KC1 or KC2, by the onium salt cannot compete with the quenching by AH: That confirms the absence of any significant role played by the onium salt in the primary process of the initiation step of the polymerization.

In KC4 and KC5, competition might occur. The yields of the KC/MDEA, KC/I0, KC/MMA interaction are evaluated according to

$$\phi_x = \frac{k_x [\text{X}]}{k_e [\text{MDEA}] + k'_e [\text{I0}] + k_q [\text{MMA}]}$$

**Table V** Rate of Polymerization  $R_p$  of MMA 7M in Acetonitrile

	$10^5 R_p$ (M s <sup>-1</sup> )
KC4 <sup>a</sup> + MDEA (0.05M)	10.8
KC4 <sup>a</sup> + MDEA (0.05M) + I0 ( $5 \times 10^{-2}$ M)	23
Eosin <sup>b</sup> + MDEA (0.05M)	7
Eosin <sup>b</sup> + MDEA (0.05M) + I0 ( $5 \times 10^{-2}$ M)	13

$\lambda \geq 400$  nm.

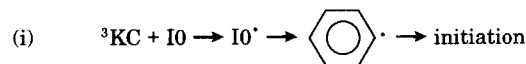
<sup>a</sup> OD ( $\lambda = 435$  nm)  $\approx 0.2$ .

<sup>b</sup> OD ( $\lambda = 546$  nm)  $\approx 0.15$ .

with  $x$  referring to MDEA or I0 or MMA; and  $k_e$ ,  $k'_e$ , and  $k_q$  are rate constants of the bimolecular quenching of  ${}^3\text{KC}$  by MDEA, I0, and MMA, respectively. In typical conditions of polymerization, the efficiency of I0 and MDEA quenching ( $k_x [\text{X}]$  are considerably higher than that by MMA). In the case of KC4 and KC5,

	$\phi_x$	
	KC4	KC5
MDEA 0.4M	0.14	0.12
I0 $5 \times 10^{-2}$ M	0.86	0.88
MMA 9M	—	—

In that case, initiation can occur through



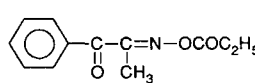
and compete with



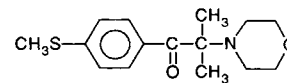
The low reactivity observed for KC4/I0 and KC5/I0 ( $D = 1 \times 10^{19}$  and  $8 \times 10^{18}$  phot cm<sup>-2</sup>) compared to KC/I0/MDEA or even KC4 or KC5/MDEA (Table VI) suggests that process (i) is less efficient than process (ii). Thus, in KC4 or KC5/I0/MDEA, the interaction between  ${}^3\text{KC}$  and I0 is not responsible for the initiation of the polymerization reaction. Electron transfer from MDEA followed by proton transfer remains the primary process leading to initiation. The detrimental effect of the addition of I0 for the yield of process (ii) is compensated for by a favorable effect on the quenching of the ketyl radicals (which leads to a decrease of the termination reactions by these radicals and, consequently, to an increase of the rate of polymerization) and the generation of phenylradicals.

### C. Photopolymerization of Multifunctional Acrylates in Film under Laser Lights

Several photosensitive systems have been tested under visible laser lights and compared with usual photoinitiators working under blue lights: DMPA, PDO, and TPMK:



PDO



TPMK

**Table VI Photopolymerization of an Acrylate Coating under Laser Light Exposure**

	$\lambda = 363 \text{ nm}$	$\lambda = 440 \text{ nm}$	$\lambda = 488 \text{ nm}$
	$10^{-17} D \text{ (phot cm}^{-2}\text{)}$		
KC4 + MDEA			9 <sup>a</sup>
KC4 + MDEA + I0			4
KC5 + MDEA			0.8
KC5 + MDEA + I0			0.2
KC5 + MDEA + PDO (5%)			1
Eosin + MDEA + PDO (5%)			4
Eosin + MDEA + I0			0.7
KC6 + MDEA			3.8
KC6 + MDEA + I0			1.6
TX5 + MDEA	8 <sup>b</sup>	8 <sup>b</sup>	
TX5 + TPMK (3%)		8 <sup>b</sup>	
DMPA	0.2 <sup>a</sup>		
DMPA	0.15 <sup>b</sup>		
DMPA + I0 (5%)	0.07		
PDO	0.25		
TPMK	0.15		

*D* is the energy absorbed by the system.

<sup>a</sup> PETA.

<sup>b</sup> E605/TMPTA (50/50). Film thickness: 30  $\mu\text{m}$ . Exposed area: 0.1  $\text{cm}^2$ . [MDEA] = 3% w/w; [I0] =  $10^{-1}M$ .

The following trends are observed (Table VI):

- a very excellent reactivity of KC,
- similar efficiency for “blue” and “visible” light-working photoinitiators, and
- addition of iodonium salt decreases the energy necessary to polymerize the sample. Addition of PDO can also do the same to a lesser extent (this has been already explained in eosin/PDO/MDEA on the basis of an effect on the initiation step<sup>20</sup>).

#### D. Photopolymerization of a Cationic Film Matrix

Sensitization of the iodonium salt decomposition in the presence of KCs or TXs is expected if one considers the data reported in Table I. Typical values for the yield of the electron transfer can be evaluated, e.g., in the system KC2/I0 ( $10^{-1}M$ )/CHO (5M) and TX1/I0/CHO:  $\approx 0.3$  and  $\approx 0.8$ , respectively. A recent work<sup>21</sup> suggests that the cationic photopolymerization of an epoxy coating in the presence of TXs and substituted iodonium salts develops very rapidly under UV light exposure.

#### IV. CONCLUSION

The results reported in this paper show that thioxanones and ketocoumarins act as very efficient photoinitiators in blue or visible laser light-induced polymerization reactions that can be used in high-tech applications such as direct laser writing of high-resolution relief patterns in imaging science and microelectronics, holographic recording and storage of information, or the manufacture of holographic optical elements. The design of three-component systems (such as ketone [e.g., ketocoumarin]–amine-onium salts<sup>6,22</sup> or dye [e.g., eosin,<sup>20</sup> xanthene dye, merocyanine<sup>23</sup>]–amine–onium salt) leads to very efficient systems. The forthcoming paper will be devoted to an investigation of the excited-state processes in this type of photosensitive combinations.

One of us (S. K. W.) thanks the Fondation pour l'Ecole Nationale Supérieure de Chimie de Mulhouse for financial support as a visiting scientist.

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Received March 27, 1991

Accepted June 17, 1991