

Development of New Dyeing Photoinitiators Based on Azomethine Dyes

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Received May 4, 1998. Revised Manuscript Received August 5, 1998

Several dyes containing the azomethine moiety have been synthesized and evaluated as photoinitiators for free radical polymerization induced with the argon-ion or He–Ne lasers. Two methods of dye modification are applied in the study. The first method is a change in the type of the substituent in the pyrazolone skeleton: methyl group (a weak electron donor) and ester group (an electron acceptor). The replacement of the substituent causes a significant red shift in the electronic absorption spectra but does not affect photoinitiation ability. Elimination or limitation of the rotation of the phenyl group (PBAD-1 and PBAD-2) causes an additional red shift and a change of the shape of the electronic absorption curve. The coplanarization of the azomethine part (ChAD) shifts to the red an absorption maximum of about 200 nm and also decreases the molar absorption coefficient. A change in the dye structure caused by the opening of the pyrazolone skeleton causes a blue shift in the absorption spectra but does not affect the photoinitiation ability. One observes a dramatic increase in the photoinitiation efficiency and an increase in the quantum yield of the bleaching process when the twisting motion of the C=N bond is severely hindered. Elimination of the motion of C=N bond by coplanarization of the azomethine residue with other parts of the dye decreases the degree of branching. This decrease in branching stabilizes the molecule in its excited state. The red shift of the absorption spectra maximum of ChAD allows the initiation of polymerization using both argon-ion and He–Ne lasers.

Introduction

In the search for systems that undergo a faster and more controllable photopolymerization, the use of visible lasers to initiate and rapidly transform a liquid monomer into a solid polymer is an important goal. In view of the recent development of dyeing initiating systems active at 488, 514, and 632 nm, both argon-ion and He–Ne lasers are used for this purpose.¹ In commercial practice, this type of photoinitiating system is limited to the Mead's Cycolor process,² applying the photochemistry of cyanine borates. The wavelength of absorption of the cyanine borate initiator is tunable by means of the number of conjugated alkene units in the cyanine dye.

Initiation of polymerization for the cyanine dye–tetraorganylborate salt involves alkyl radical formation as a result of photoinduced electron transfer from borate anion to the singlet state of the cyanine cation. The process involves a short-lived excited singlet state; therefore, the initiation abilities of cyanine dyes are much lower compared with the photoreactivity of xanthene dyes studied by Neckers group.³ Other visible-light-induced compositions contain camphorquinones, which are commonly used for the polymerization of dental restorative formulations.⁴

In our earlier paper⁵ we presented a new class of free radical photoinitiators based on pyrazolone azomethine (PAM) dyes. It was stated that a control test with Rose bengal derivative (RBAX)^{3a} showed that PAM dyes initiate free radical polymerization at a much slower rate. Therefore, in this paper, it is our intention to present studies illustrating the relationship between structures of PAMs and their photoinitiation ability, especially studies demonstrating the relationship between the freedom of rotation of azomethine dye fragments and photoinitiation activity.

Experimental Section

Substrates used for the preparation of dyes were purchased from Fluka, Merck or Aldrich. Pentaerythritol triacrylate (PETA), 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), 1-methyl-2-pyrrolidinone (MP), and *N*-phenylglycine (NPG) were purchased from Aldrich.

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(2) Cycolor is a trademark of Mead Corp. The name of process indicates the type of dye used as a primary absorber.

All dyes tested were prepared by methods described elsewhere.⁶ The crude dyes were purified by column chromatography and finally by preparative thin-layer chromatography (TLC). The final products were identified by ¹H and ¹³C NMR spectroscopy. The spectra obtained were evidence that the dyes were of the desired structures.

Absorption spectra were obtained with a Varian Cary 3E spectrophotometer. Fluorescence spectra were recorded with a Hitachi F-4500 spectrofluorimeter. All spectra were obtained in ethyl acetate solution.

The kinetics of free radical polymerization were studied with a polymerization solution composed of 1 mL of MP and 9 mL of PETA or TMPTA. Dye concentration was varied from 1×10^{-4} to 5×10^{-4} M; the concentration of NPG was also varied from 0.05 to 0.1 M. The concentration of the azomethine part (ChAD) in compositions used for real-time infrared (RTIR) measurements were 0.1 M. Before curing, the polymerizing mixture was not deaerated.

The kinetics of polymerization were determined by measuring the polymerization heat evolution of a sample (irradiated with laser beam through an optical system) in a homemade microcalorimeter.⁷ A temperature sensor, a semiconducting diode immersed in the 2-mm thick layer (about 290 mg) of cured sample, was used for detection of the heat flow. Amplified signals were transformed with an analog/digital data acquisition board to a computer. To avoid the possibility of nonisothermal reaction conditions, for further discussion, only the data for initial time of polymerization were used for the calculation of the polymerization rates.

The second method, RTIR,⁸⁻¹⁰ allowed the rate of the monomer double bond disappearance to be monitored in real time. The IR spectrometer (Secord-IR 71, Carl-Zeiss Jena) was set in the transmission mode, and the detection wavelength was fixed at a value where the monomer double bond exhibits a discrete and intense absorption [e.g., at 810 cm^{-1} for acrylic monomers (CH=CH₂ twisting)]. The signal was transformed with an analog/digital data acquisition board to a computer. A thin monomer film (transmittance at 810 cm^{-1} in a range of 90%) was coated onto a polyethylene sheet and placed between NaCl salt disks.

Irradiation of the polymerization mixture was carried out using the emission of an Omnichrome Model 543-500 MA argon-ion laser or the emission of a Melles Griot He-Ne 30 mW laser (632.8 nm). The light intensity was measured by a Coherent Model Fieldmaster power meter.

The reduction potentials of the dyes were measured by cyclic voltammetry. An Electroanalytical Cypress System Model CS-1090 was used for measurements, and Ag-AgCl electrode served as a reference electrode. The supporting electrolyte was 0.5 M tetrabutylammonium perchlorate.

Results and Discussion

Several targets in developing visible dye photoinitiators are important. First, shifting the dye absorption to the red, and second, increasing the rate of polymerization photoinitiation to near-photographic speed. Also, solubility in monomers, dark stability, and harmlessness are still main topics of consideration. Azomethine dyes are commonly used in color photography. PAM dyes are prepared during the developing process in color photography, therefore their earlier mentioned properties (e.g. dark stability, color loss, and harmlessness) are well-known.

The analysis of the kinetic scheme for photoinduced polymerization via an intermolecular electron-transfer process has shown⁷ that the following equation can describe the rate of polymerization in viscous media:

$$R_p = k_p[M] \left[\frac{2I_a \Phi_T k_{el} - k_{bl} [D \cdots \dot{A}H]}{k_t} \right]^{0.5} \quad (1)$$

where I_a is intensity of absorbed light, Φ_T is the quantum yield of triplet state formation. The rate of free radicals cross-coupling, yielding the dye bleaching products, is denoted by k_{bl} , k_p and k_t denote the rates constants of polymerization and chain termination steps, respectively, and k_{el} is the first-order rate constant of electron transfer described by the Eyring equation

$$k_{el} = \chi Z \exp(-\Delta G^\ddagger/RT) \quad (2)$$

where Z is a frequency factor, χ is the transmission coefficient, and ΔG^\ddagger is the free energy of activation given by the Marcus¹¹ equation for neutral reactants

$$\Delta G^\ddagger = \frac{\lambda}{4} \left(1 + \frac{\Delta G_{el}^\circ}{\lambda} \right)^2 \quad (3)$$

where λ is the reorganization energy necessary to reach the transition states both of excited molecules and of solvent molecules, and ΔG° is expressed by the Rehm-Weller equation¹²

$$\Delta G_{el}^\circ = E_{ox}(D/D^+) - E_{red}(A^*/A) - Z e^2/\epsilon a - E_{00} \quad (4)$$

where $E_{ox}(D/D^+)$ is the oxidation potential of the electron donor, $E_{red}(A^*/A)$ is the reduction potential of the electron acceptor, E_{00} is the excited-state energy, and $Z e^2/\epsilon a$ is the Coulombic energy, which is considered negligible with respect to the overall magnitude of the ΔG in the present system.

Summarizing the analysis just presented, one can conclude that to compare the rates of free radical initiated polymerization for different photoinitiators, several principal requirements should be considered. First, the rate of photoinitiated free radical polymerization depends on the yield of triplet state formation. Second, it depends on both the thermodynamical (ΔG°) and kinetic (λ) aspects of the electron-transfer process. Third, it may depend on the reactivity of free radicals resulting from the electron-transfer process.¹³

The PAM dyes are so-called branched dyes. Their fluorescence (if observable) quantum yields are very small. Therefore, the fluorescence properties cannot be a measure of photoinitiation efficiency. The short lifetime of the singlet excited state and low quantum yield of intersystem crossing¹⁴ of PAM dyes is probably due to the high freedom of rotation around bonds linking each part of the molecule with the pyrazolone skeleton.

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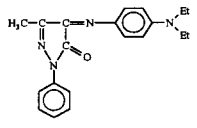
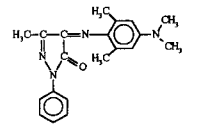
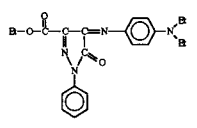
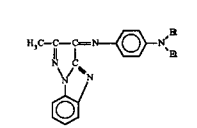
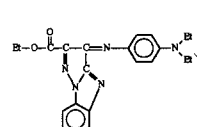
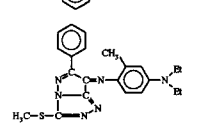
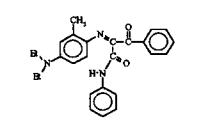
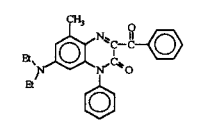
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Table 1. Structures and Basic Spectroscopic and Electrochemical Properties of Dyes Tested

Structure	λ_1 [nm]	λ_2 [nm]	ϵ_{λ_1}	ϵ_{λ_2}	$Fl_{\lambda_{max}}$ [nm]	E_T^{**} kcal/mol	E_{red} [V]	ΔG° [eV]	
	PAD-1	515	441	35000	16000	N.O.*	44	-1.020	-0.225
	PAD-1d	640	---	12000	---	N.O.*	45	---	---
	PAD-18	552	462	39000	14500	CT 585	---	-0.722 -1.168	---
	PBAD-1	530	---	38600	---	CT 585	---	-1.070	---
	PBAD-2	574	---	39000	---	N.O.	---	---	---
	PTAD	564	---	53800	---	only LE 495, 515	24-28	-0.982	0.490
	BAAD	433	---	16000	---	only LE 520	41-45	-1.110	-0.120
	ChAD	643	---	6000	---	only LE 520	44	-1.208	-0.067

N.O.* - not observable, ** lit. poz. 17

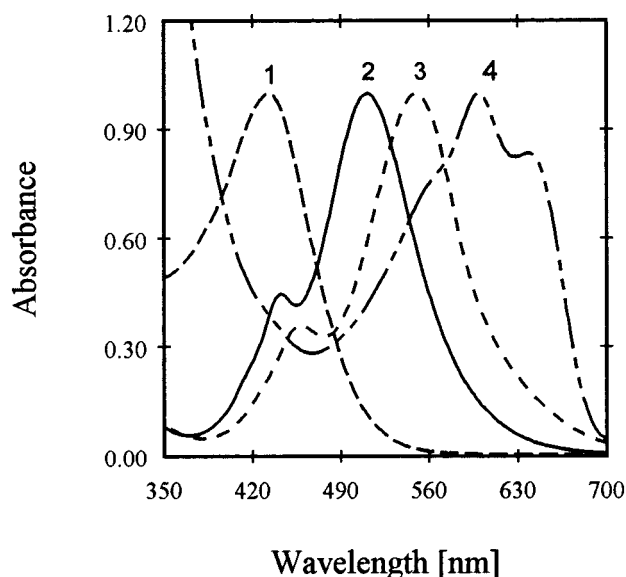
**Figure 1.** Electronic absorption spectra of (1) BAAD, (2) PAD-1, (3) PAD-18, and (4) ChAD in ethyl acetate.

Figure 1 shows the electronic absorption spectra of dyes tested. Figure 2 presents the emission properties

of selected dyes and Table 1 summarizes the structures and spectroscopic and electrochemical data.

The electronic absorption spectra of each of the dyes show an absorption in a visible region due to the presence of azomethine residue conjugated either with pyrazolone, pyrazolo-*s*-triazolo, benzoylacetanilide, or quinoxalone-2 moieties.

The PAM dyes show a characteristic double absorption band (see Figure 1). The change in the dye structure by elimination of the rotational freedom of selected parts of the dye causes changes in their electronic absorption spectra. The changes are demonstrated by both the distinct red or blue shift and an alteration in the absorption curve structure. The modification of the dye structure also affects their emission properties and reduction potentials.

Only two tested dyes (PAD-18 and PBAD-1) exhibit weak emission when excited at the charge transfer (CT) transition band (see Figure 2). All tested dyes fluoresce weakly from locally excited states (excitation in the region 400–450 nm). Fluorescence emission measurements clearly show that the fluorescence properties cannot be used for the prediction of the photoinitiation ability of tested dyes.

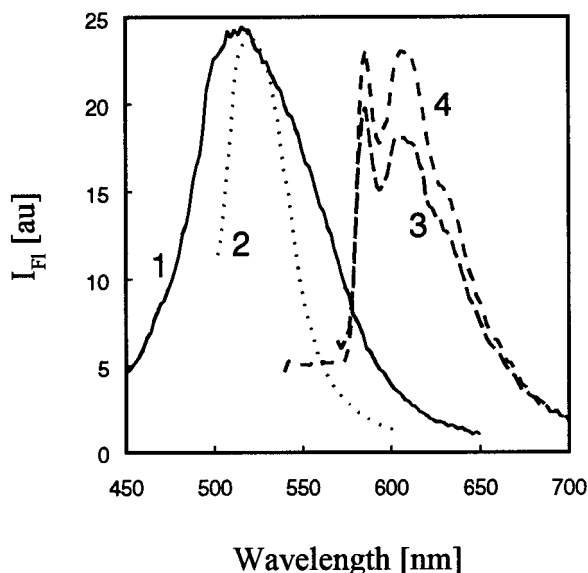


Figure 2. Fluorescence emission spectra of dyes tested in ethyl acetate. (1) BAAD, (2) PBAD-1, (3) PAD-18, and (4) ChAD.

Two methods of dye modification are applied in our study. The first is the change of the character of the substituent in the pyrazolone skeleton. Two different groups were tested; the methyl group (a weak electron donor) and an ester group (an electron acceptor). The replacement of the methyl group by an ester group causes a significant red shift in the electronic absorption spectra. There is only a slight effect of the type of the substituent in the pyrazolone skeleton on the reduction potential of the dyes. Elimination or limitation of the rotation of the phenyl group (PBAD-1 and PBAD-2) causes an additional red shift and a change of the electronic absorption curve. The formation of a planar and rigid azomethine moiety (ChAD) causes significant change in the absorption spectra. The coplanarization of the azomethine part shifts to the red the absorption maximum of about 200 nm and additionally decreases the molar absorption coefficient. This result is important in view of the laser-initiated polymerization occurring at a depth below the surface plane of a highly functionalized cross-linkable monomer.

To move the front of the polymerization deeper below the polymerizing mixture surface plane, the absorbance of the initiator must disappear.¹⁵ Visible irradiation of the tested dyes in moderate polar solvents and in the absence of any additives do not change their absorption spectra. However, after the addition of an effective electron donor, one sees, during irradiation, distinct changes in the electronic absorption spectra. This phenomenon is illustrated in Figure 3.

The influence of the dye structure on their polymerization photoinitiation ability is very significant. As Figure 4 shows, the best photoinitiation capability presents ChAD. Its sensitivity is comparable to the sensitivity of the novel xanthene dyes studied by Neckers^{3b,d,e} or well-known cyanine borates described by Schuster et al.¹ The red shift of the electronic absorption spectra of ChAD allows for the initiation of

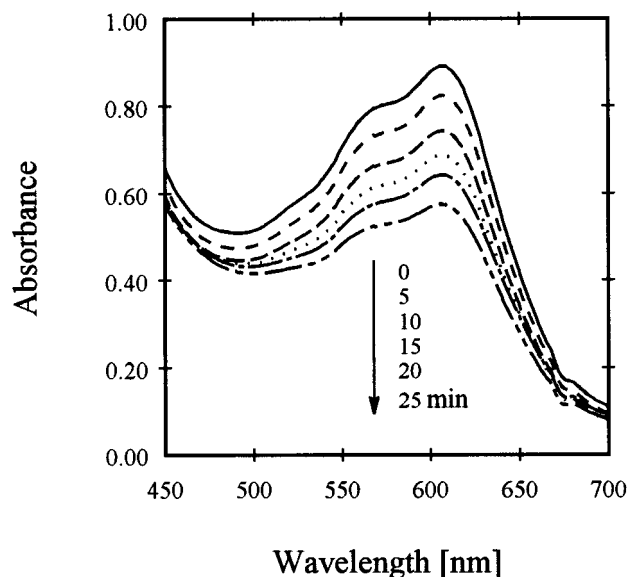


Figure 3. Changes of the electronic absorption spectra of ChAD in the presence of *N*-phenylglycine (0.1 M) in ethyl acetate during argon-ion laser irradiation ($I_a = 300$ mW).

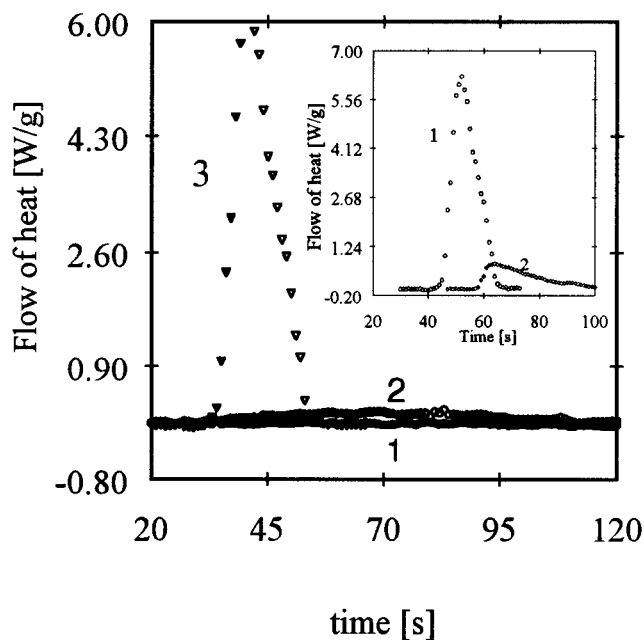


Figure 4. The flow of heat (thick layer method) during argon-ion laser-initiated polymerization of pentaerythritol triacrylate (PETA) in the presence of *N*-phenylglycine (0.1 M; $I_a = 300$ mW). Dyes tested (10^{-3} M): (1) PAD-1, (2) BAAD, and (3) ChAD. Inset: The flow of heat during laser-initiated polymerization of PETA. Initiating system: (1) ChAD-NPG and (2) cyanine borate initiating ion pair ($I_a = 300$ mW). (see ref 1 and Kabatc, J.; Pietrzak, M.; Pączkowski, J. *Macromolecules* **1998**, *31*, 4651).

polymerization using both argon-ion and He-Ne lasers (see Figure 5).

The dyes tested were selected in a way that allows the elimination or the reduction of the rotational freedom of selected parts of the molecule. This change can eliminate or reduce the channels of the excited states deactivation, causing a decrease in photoinitiation ability. As can be seen in Table 1, in the case of PAD-1d there is a steric hindrance that may reduce the freedom of rotation of the phenyl group of azomethine moiety. However, according to Herkstroeter,¹⁶ the

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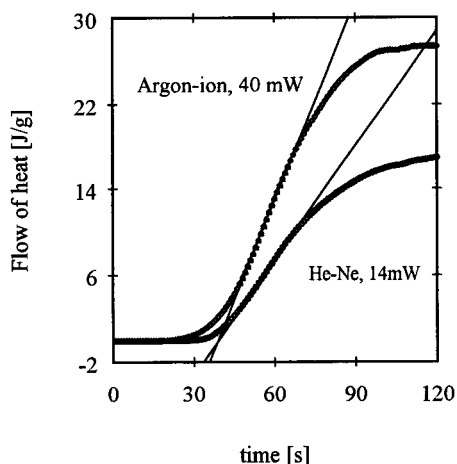
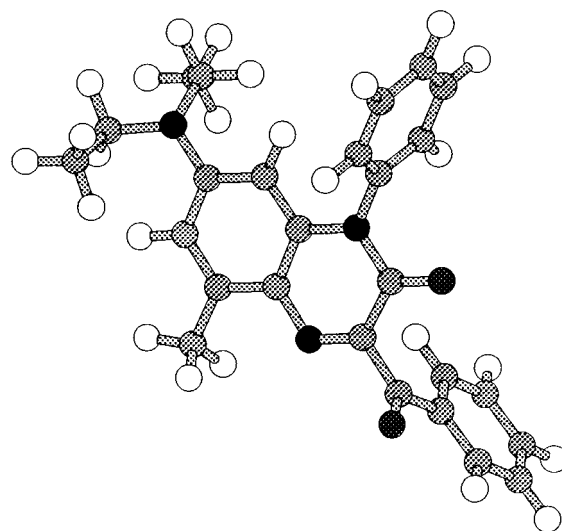


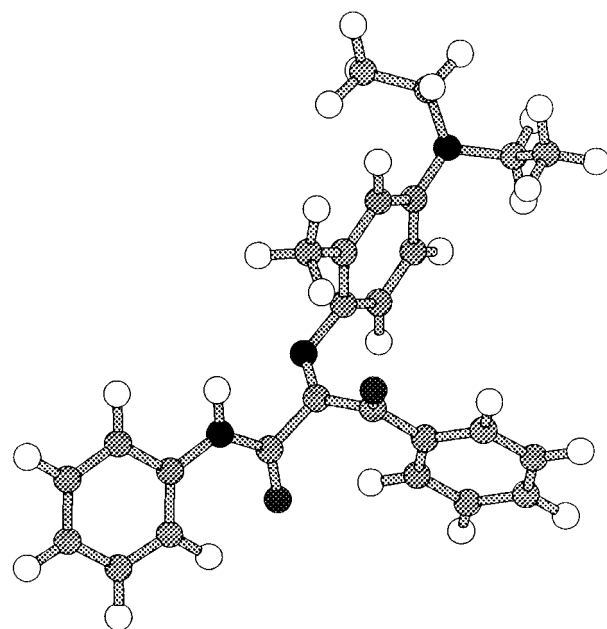
Figure 5. The flow of heat (thick-layer method) during laser-initiated polymerization of trimethylolpropane triacrylate (TMPTA). Initiating system ChAD (10^{-3} M)–*N*-phenylglycine (0.1 M). Laser type indicated in figure.

introduction of the methyl groups into the ortho positions of the aromatic ring, attached to the azomethine nitrogen atom, accelerates the rate of azomethine group isomerization. This acceleration is probably why PAD-1d is an ineffective sensitizer of photoinduced polymerization. There is also no effect on photoefficiency when one changes the type of substituent at the pyrazolone skeleton from an electron-donating ($-\text{CH}_3$) to an electron-accepting ($-\text{C}(\text{O})\text{OEt}$) group. In addition, the elimination of the rotation of phenyl residue linked to the pyrazolone skeleton does not cause any increase in the sensitivity. A similar effect is observed when the pyrazolone moiety is additionally rigidized by a *s*-triazole ring. The change in the dye structure by the opening of the pyrazolone skeleton causes a blue shift in the absorption spectra but does not affect the photoinitiation ability. One observes a dramatic increase in the photoinitiation efficiency (by 2 orders of magnitude) when the twisting motion of $\text{C}=\text{N}$ bond is severely hindered by structural constraints. Elimination of the motion of $\text{C}=\text{N}$ bond by coplanarization of the azomethine residue with other parts of the dye (see Figure 6) decreases the degree of branching of the dye, which stabilizes the molecule in its excited state. This distinct effect is easy to interpret in terms of the activation energies needed for aromatic imine isomerization, which is on order of 20 kcal/mol or less.¹⁶ One more important conclusion arises from the analysis presented; that is, the rotation around $\text{C}=\text{N}$ bond is the main channel of the excited-state deactivation for azomethine dyes.

According to Herkstroeter,¹⁷ the triplet energy levels in azomethine dyes are not observed directly. The measurement of the dye triplet state energy is possible by an indirect method. PADs do not sensitize the singlet oxygen formation,¹⁸ instead they are good singlet oxygen quenchers. This result is probably because of very low quantum efficiency of intersystem crossing. In this connection, it is interesting to compare the sensitizing efficiency and the quenching abilities of singlet oxygen



a



b

Figure 6. The optimized nuclear configurations of (a) ChAD and (b) BAAD. Optimization performed using Hyper-Chem v.4, AM1 method.

by BAAD and ChAD. ChAD differs from BAAD by the presence of a bond from the amide nitrogen of the aromatic ring coming from the developer.¹⁹ For the studied dye, an additional band is introduced by the modification of the developer in a way allowing the formation of the bond between the pyrazolone skeleton and the developer residue. This bond prevents the rotation of the $\text{C}=\text{N}$ bond. As a result, ChAD is a sensitizer when BAAD is a singlet oxygen quencher. The triplet lifetime of ChAD is on order of 80 μs , whereas

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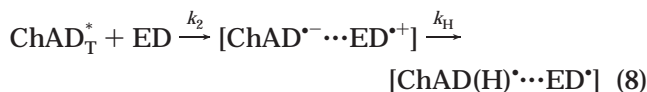
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(19) For classical system, development involves reduction of the silver and, in color photography, it is the consequent oxidation of the developer that reacts with color coupler to produce an image dye. A typical system involves a derivative of benzene-1,4-diamine as developer; see: Wayne, R. P. *Principles and Applications of Photochemistry*; Oxford University: Oxford, 1988.

the triplet lifetime for BAAD is $<10 \mu\text{s}$.¹⁴ This energy dissipation channel is desired for azomethine dyes used for color photography but is not needed for other photochemical applications, such as the sensitization of singlet oxygen formation or the sensitization of the polymerization via the photoinduced electron-transfer process.

For ChAD, the relationship between the rate of polymerization and intensity of irradiation is very specific. From Figure 7 it is easy to deduce that the rate of polymerization varies linearly with the light intensity. Classical treatment of the kinetics for free radical polymerization predicts that the rate of polymerization should increase linearly with the square root of the light intensity.

There are several possible explanations of the observed phenomenon. For the high degree of cross-linking, radical trapping is likely the dominating mechanism. However, in our experiments, we are recording the initial rate of polymerization. Therefore, this explanation should be rejected. The second possible explanation concerns the properties of the dye-initiating system. For the explanation, one should consider the effective channels of the dye photoreductions. The kinetics of the polymerization induced via photoinduced intermolecular polymerization can be described as follows



From the kinetic scheme, and considering S as an irradiation area, neglecting diffusion effect, and knowing that all light is absorbed by the irradiated mixture, one can describe the disappearance of the dye as follows

$$-\frac{d[\text{Dye}]}{dt} = I_0 \Phi_T S \frac{k_{bl} + k_p}{k_1 + k_2 + k_{bl} + k_p} \quad (11)$$

The decrease of the dye concentration can be also expressed as a part of the solution volume where the dye is disappeared completely,

$$-d[\text{Dye}] = S d l [\text{Dye}] \quad (12)$$

where l is the z direction of the process. The combination of eqs 11 and 12 gives

$$dV = S d l = \frac{I_0 \Phi_T}{[\text{Dye}]} \frac{k_{bl} + k_p}{k_1 + k_2 + k_{bl} + k_p} dt \quad (13)$$

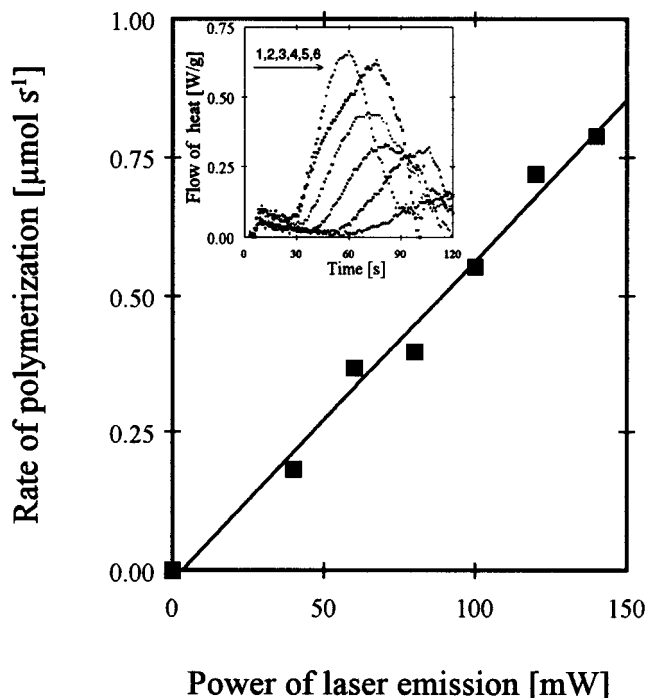


Figure 7. Rate of polymerization of trimethylolpropane triacrylate (TMPTA) as a function of light intensity measured using the thick-layer method measurement (flow of heat measurement). Initiation system: ChAD-NPG.

For a given dye, electron donor and monomer, and for the initial time of polymerization, $k_{bl} + k_p/k_1 + k_2 + k_{bl} + k_p$ is constant. Equation 13 clearly shows that the bleached volume of the irradiated system is directly proportional to the light intensity. It is obvious that polymerization at a certain depth is possible when the dye bleaches. From eq 13, one can deduce that the change of the depth (d) of polymerization is controlled by the rate of the bleaching process, and that this process is directly proportional to the light intensity. To verify this supposition, the RTIR measurements of the rate of polymerization were performed. RTIR methodology requires very thin films, which limits the absorption of the irradiated mixture (absorption of the initiating system <0.1). Under this condition, the rate of polymerization cannot be limited by the rate of the bleaching process. Results of the RTIR measurements are summarized in Figure 8.

Experiments performed with different power densities in the range from 30 to 175 mW/0.785 cm² indicate that for thin film, the rate of polymerization also varies proportionally with the light intensity. Therefore, based on thick-layer and thin-film measurements, we conclude that in our system, the rate of polymerization is not controlled by the rate of the bleaching process and that the termination occurs not from the reaction between the two polymer radicals but between one macroradical and one radical being produced from the dye photoinitiator. It is important to note that the monoradical termination is typical for monomers forming cross-linked products at a low degree of polymerization; for example, for the system that formed radical trapping from the very beginning of the photopolymerization process.²⁰ For the initial time of polymerization of the monomer used in our study, the monoradical termination can be excluded because the tests performed for

Table 2. Quantum Yields of Bleaching (Φ_{bl}), Rates of Bleaching (k_{bl}), and Rates of Photoinitiated Polymerization (R_p) for Dyes Tested

dye	PAD-1	PAD-1d	PAD-18	PBAD-1	PBAD-2	PTAD	BAAD	ChAD
Φ_{bl}	2.06×10^{-6}	1.15×10^{-7}	95×10^{-6}	2.25×10^{-6}	98.8×10^{-6}	6.34×10^{-6}	15.74×10^{-6}	1.29×10^{-3}
$R_p \times 10^3$ ($\mu\text{mol/s}$)	2.63	n.o. ^a	2.40	6.57	3.70	3.76	22.7	787
$k_{bl} \times 10^{-5}$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	2.60	—	108	2.75	145	10.2	8.50	—

^a n.o., not observable.

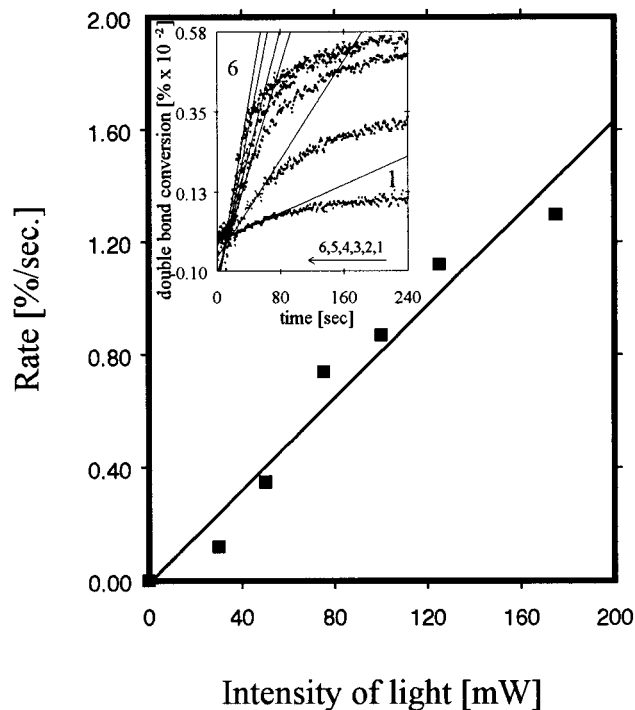


Figure 8. Rate of polymerization of trimethylolpropane triacrylate (TMPTA) as a function of light intensity measured using the RTIR spectroscopy method (thin film). Initiation system: ChAD-NPG.

cyanine dyes and anionic borate salts show, for identical monomeric mixture, results indicating typical bimolecular termination (e.g., the order of polymerization rate with respect of light intensity is 0.5^{21}).

Because visible initiators often bleach as they generate reaction intermediates, it was interesting to ascer-

tain whether there is a relationship between the polymerization photoinitiation ability and the quantum yield of the bleaching process. The data illustrating the above-mentioned relation are presented in Table 2. Inspection of the data in Table 2 shows a certain regularity. The dyes displaying low polymerization photoinitiation ability also bleach with very low quantum yield and, as the efficiency of initiation increases, one can also see a sharp increase in the dye bleaching quantum yield. This relationship clearly shows that the bleaching process is a competition channel scavenging the free radicals during the initiation of polymerization.

The initiator efficiency, according to classical theory of photoinduced electron transfer, depends on a thermodynamic driving force process and the kinetic parameters of the process (e.g., it depends on the factors described by the Marcus theory). Analysis of the data from Table 1 shows that there is no relationship between free energy of activation of ET and the rate of photoinitiated polymerization. This result is probably because of different quantum yields of triplet formation for each dye and variations in the triplet lifetimes, as shown for BAAD and ChAD.

Acknowledgments. This research was sponsored by the State Committee for Scientific Research (KBN) Poland (grants no. 3 T09A 012 11 and BW-21/93).

CM9803197

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