

Pyrazolone azomethine dyes as effective photoinitiators of free radical polymerization

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A new class of free radical photoinitiators based on pyrazolone azomethine dyes has been investigated. Results show that the free radical formation occurs via intermolecular electron transfer. Changes in the dye structures are translated into changes in the rate of polymerization. Dyes which have electron withdrawing substituents initiate the free radical polymerization more readily than those with electron releasing groups. The introduction of heavy atoms into the dye molecule decreases the rate of initiation of free radical polymerization.

(Keywords: dye initiating system; pyrazolone azomethine dyes)

INTRODUCTION

In photopolymerization, the initiating free radicals are formed by photoprocessing. The majority of photopolymerizable compositions used in industry are sensitive to u.v. light.

Panchromatic sensitization of vinyl polymerization requires the presence of suitable dyes as primary absorbers of light. Photophysical energy transfer between the excited state of the initial dye and other chromophores, which would yield free radical initiating species, is generally energetically unfavourable. A non-classical endothermic energy transfer process is required. An electron transfer process represents such an alternative¹, in which the excited sensitizer, S*, functions as an electron acceptor. In the presence of a suitable electron donor, D, reduction of S* produces cation radical D+• which may be transferred into the species initiating polymerization.

In 1954 Oster² was the first to report a dye-sensitized system and identified several classes of effective dyes, among them acridine, xanthene and thiazine dyes. In recent years more detailed research has concentrated on the properties of xanthene dyes³⁻⁶. However, Cycolor (Mead Corporation, USA) was the first commercial product of which we are aware to use a visible light system, applying cyanine borates⁷ as a visible light initiating system.

In the search for a new visible light initiating system, we have developed a new group of visible light photoinitiators based on pyrazolone azomethine dyes.

EXPERIMENTAL

Substrates used for the preparation of dyes were purchased from Fluka, Merck or Aldrich. Pentaerythritol triacrylate (PTA), *N*-phenylglycine (NPG), 1-methyl-2-pyrrolidone (MP) were purchased from Aldrich.

All dyes tested were prepared using methods described elsewhere⁸. The crude dyes were purified using column chromatography and finally by preparative thin layer chromatography. The final products were identified by ¹H n.m.r. spectroscopy. The spectra obtained and the melting points observed⁹ were evidence that the dyes were of the desired structures.

The kinetics of polymerization were studied using a polymerizing solution composed of 1 ml of MP and 9 ml of PTA. Dye concentration was varied from 1×10^{-4} to 5×10^{-4} mol l⁻¹; concentration of NPG was also varied from 0.05 to 0.15 mol l⁻¹.

Irradiation of the polymerization mixtures was carried out using the entire visible emission spectrum from a xenon lamp (Philips CSX 150 W/1) with total intensity of light, $I = 5.17 \times 10^{-8}$ einsteins cm⁻² s⁻¹. The visible light intensity was measured using Reinecke's salt K₃Cr(NCS)₆ as an actinometer^{10,11}.

Photopolymerization in the thick film was carried out using apparatus that permitted measurement of the rate of heat evolution in a sample 2–3 mm thick. A semiconducting diode (1 mm diameter) was used as a detector.

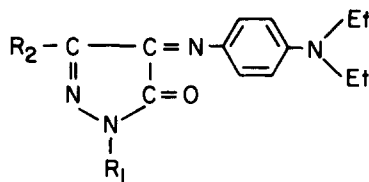
RESULTS AND DISCUSSION

Pyrazolone azomethine (PAM) dyes are commonly used in colour photography¹², consequently the research related to the chemistry of these dyes is centred on the stability and photochemistry of the bleaching processes^{13,14}.

PAM dyes are prepared during the developing process in colour photography. For laboratory application, the dyes were prepared by reaction of pyrazolone with the oxidized form of *p*-phenylenediamine⁸. The structures of the dyes tested are presented in Scheme 1. R₁ and R₂ are listed in Table 1.

In the electronic absorption spectra of PAM dyes, a large part of the visible area is accompanied by the characteristic double absorption band (see Figure 1). The

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Scheme 1

half-width of the main absorption band oscillates between 3000 and 4000 cm^{-1} . The shape and position of the absorption bands allow the use of common argon ion (514 nm) or even helium/neon (632.8 nm) lasers for the initiation. The electronic absorption data are summarized in Table 1.

Irradiation in ethyl acetate of PAM dyes in the presence of NPG causes dye loss¹⁵. This observation suggests that the PAM-NPG system may initiate free radical polymerization. The rate of heat evolution during polymerization, measured for the thick film (2–3 mm) monomer–initiator mixture, was used to study and to classify the initiation ability. The thick film measurements, in contrast to the thin foil calorimetry¹⁶, simulates the conditions found in stereolithography^{17–20}. Because of photoinitiator bleaching, the initiation process may occur at depth, and irradiation generates a solid thick film, the thickness of which depends on the exposure. Figure 2 shows the rate of heat evolution (in arbitrary units) during a photopolymerization experiment. The shape of the curve observed for the thick film polymerization differs slightly from those obtained in thin foil calorimetry^{5,16}. Since the free radical polymerization front moves as irradiation is continued, the heat evolution in thick film experiments is a more continuous process. For determination of the initiation ability, the slope observed for the initial time of irradiation was applied. Assuming the lowest slope as a standard sensitivity, $S = 1$, one can

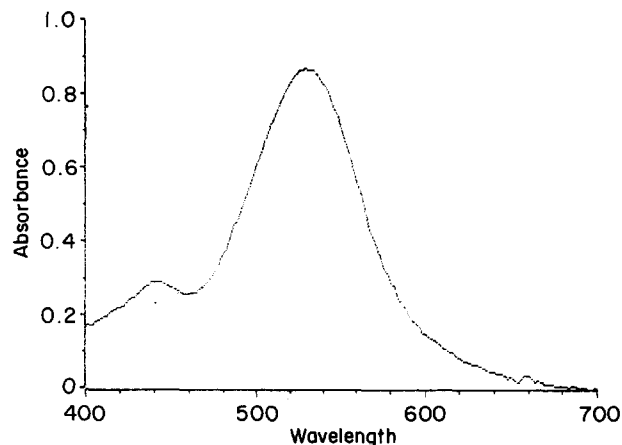


Figure 1 Visible absorption spectra of XII in ethyl acetate

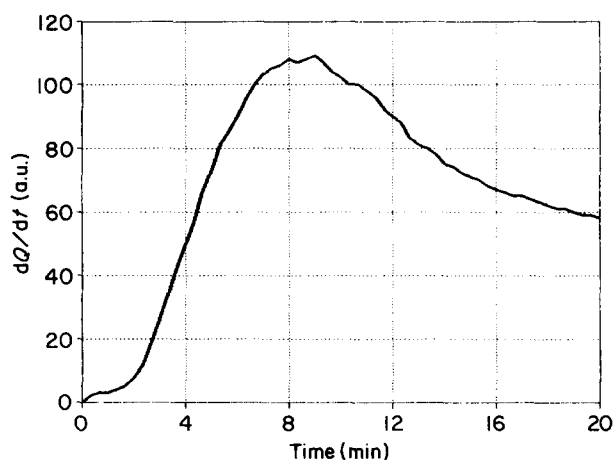

 Figure 2 Rate of heat evolution during the polymerization of PTA-MP (9:1) mixture initiated by VI, $[\text{NPG}] = 0.05 \text{ mol l}^{-1}$

Table 1 Spectroscopic and photochemical characteristics of tested pyrazolone azomethine dyes

No.	R ₁	R ₂	λ_1 (nm)	λ_2 (nm)	ϵ_{λ_1}	ϵ_{λ_2}	$\epsilon_{\lambda_2}/\epsilon_{\lambda_1}$	Relative sensitivity
I	Ph	–CH ₃	520	441	35 000	14 000	0.40	1.60
II	Ph	–NH ₂	503	424	39 000	9400	0.241	1.00
III	Ph	–NH–Ph	515	427	44 000	7800	0.177	1.15
IV	Ph	–NHC(O)Ph	527	436	46 000	7200	0.156	2.35
V	Ph	–NHC(O)NHPH	532	432	53 500	6200	0.116	1.20
VI	Ph(Cl) ₃	–CH ₃	533	437	38 000	9500	0.25	4.85
VII	Ph(Cl) ₃	–NH ₂	506	416	42 000	7200	0.171	1.20
VIII	Ph(Cl) ₃	–NH–Ph	520	420	48 500	6300	0.130	3.85
IX	Ph(Cl) ₃	–NHC(O)Ph	534	434	50 500	6100	0.121	4.20
X	Ph(Cl) ₃	–NHC(O)NHPH	537	426	55 000	5900	0.109	3.10
XI	NHCOCH ₃ 	–CH ₃	543	438	39 500	7800	0.197	2.50
XII	p-I–Ph–	–CH ₃	517	429	36 000		0.422	2.35
XIII	 SO ₂ CH = CHCl	–CH ₃	524		45 000			2.60
XIV	Ph(Br) ₃	–CH ₃	522		28 000			2.45

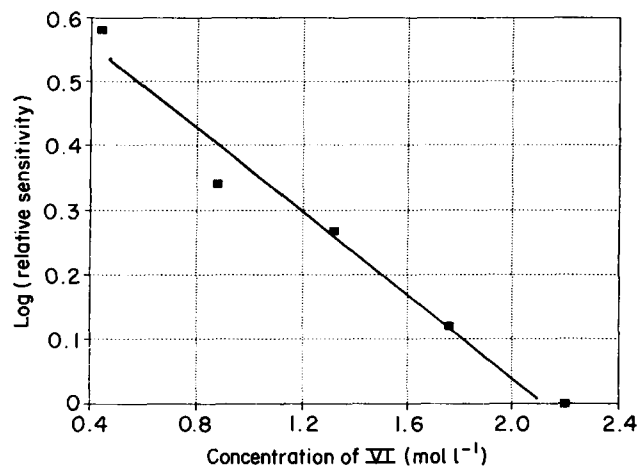


Figure 3 Effect of dye (VI) concentration on the relative rate of polymerization: PTA-MP (9:1), [NPG] = 0.05 mol l⁻¹

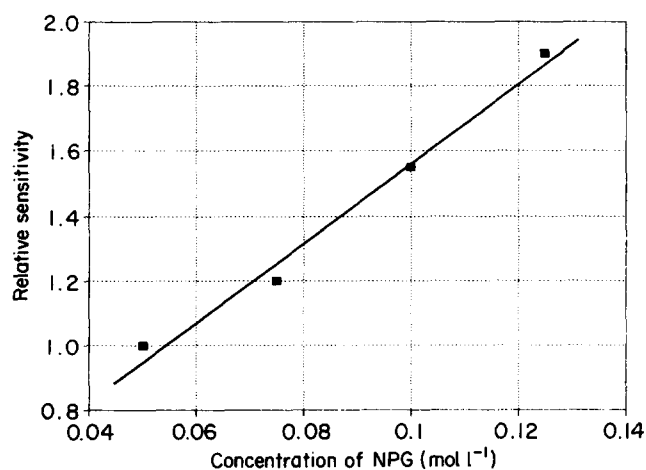


Figure 4 Effect of NPG concentration on the relative rate of polymerization: [VI] = 2.10 × 10⁻⁴ mol l⁻¹, PTA-MP (9:1)

calculate the relative sensitivity for all dyes tested. The sensitivity data are also summarized in Table 1.

Supplementary experiments were performed for various initiator (Figure 3) and coinitiator (Figure 4) concentrations. For comparison, a control test using Rose Bengal derivative (RBAX) was also carried out⁵. Results obtained for the PAM-NPG system, the supplementary experiments and the control test allow the following conclusions to be drawn.

The PAM dyes are effective visible light initiators. In the absence of NPG, irradiation does not cause any polymerization. This suggests that the photochemical mechanism involves an intermolecular electron transfer process⁷.

The relationship between the relative sensitivity and coinitiator concentration suggests that the electron transfer process occurs between a short-lived excited state in the dye, e.g. singlet excited state, and an electron donor (NPG).

The introduction of heavy atoms to a dye molecule decreases the initiation efficiency. This observation provides additional evidence that electron transfer occurs

via the singlet excited state. The formation of the triplet excited state is a more photochemically unreactive pathway than the singlet excited state deactivation.

The changes in the dye structures are translated into changes in the rate of polymerization. Dyes with electron withdrawing substituents (R₁ and R₂) initiate the free radical polymerization more easily than those with electron releasing groups. These observations are consistent with the data observed by Chen²¹ for thiazine dyes and with the theory that the rate determining electron transfer is important in this process.

The negative slope for the relationship between the logarithm of relative sensitivity and concentration of the dye is not related to the dye aggregation (in this case a Stern-Volmer-like relationship should be observed), but arises from the depth of light penetration. This is why the thin foil and thick film photocalorimetry are not comparable.

A control test with Rose Bengal derivative showed that PAM dyes initiate free radical polymerization with a rate one order of magnitude lower than RBAX. However, in contrast to the Rose Bengal derivatives, the PAM dyes do not fluoresce. Fluorescence of the initiating dyes dramatically decreases the resolution (by means of reabsorption and re-emission processes) of the three-dimensional image and additionally causes a sticky surface of the three-dimensional subject. The accessibility of high power visible light lasers partly reduces the disadvantage of low sensitivity and may enable the use of PAM dyes as effective initiators in stereolithography.

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