ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 128 (1999) 135–138

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

3-Benzoyl-7-diethylamino-5-methyl-1-phenyl-1H-quinoxalin-2-one: an effective dyeing photoinitiator for free radical polymerization

Zdzisław Kucybała, Jerzy Pączkowski *

University of Technology and Agriculture, Faculty of Chemical Technology and Engineering, Seminaryjna 3, 85-326 Bydgoszcz, Poland

Received 29 June 1999; accepted 20 July 1999

Abstract

3-Benzoyl-7-diethylamino-5-methyl-1-phenyl-1H-quinoxalin-2-one (**ChAD**) is, in the presence of the effective electron donors, good dyeing free radical polymerization initiator. Photoinitiation ability of the tested dye strongly depends on the type of *N*-phenylglycine derivative used as an electron donor. The results show that the rate of polymerization can be described as the linear function of either free energy of activation for electron transfer process (ΔG^0_{ET}) or as a linear dependence of the reactivity of the free radicals obtained as a result of secondary processes that are following electron transfer. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Dyeing photoinitiator; Kinetics of photoinduced polymerization; Effect of the coinitiator

1. Introduction

Pyrazolone (PADs) and benzoylacetanilide (BADs) azomethine dyes are commonly used in color photography as one of the color-picture forming dyes [1,2]. Using standard organic chemistry, one can obtain in solution PADs or BADs displaying a wide range of color, starting from yellow to green [2–7]. In an earlier paper [8], we have shown that purple PADs can photoinitiate free-radical polymerization via a photoinduced intermolecular electron transfer process. For a better evaluation of the photochemistry of azomethine dyes, the modification of the dye that restricts the rotational freedom of selected parts of the molecule was applied. This approach can eliminate or reduce the channels of the excited-state deactivation which can cause a change in the rate of dye polymerization photoinitiation ability. Several specific dyes containing the azomethine residue conjugated either with pyrazolone, pyrazolobenzimidazole, pyrazolo-s-triazolo, benzoyloacetanilide or quinoxalone-2 moieties were prepared [9]. In this paper we present the more detailed results of a study on the novel, effective, dyeing free radical polymerization initiator that can be initiated by both argon-ion and He–Ne lasers.

2. Experimental

Substrates used for the preparation of dye were purchased from Aldrich. 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), 1-methyl-2-pyrrolidinone (MP), *N*-phenylglycine (NPG) were also purchased from Aldrich. *N*-phenylglycine derivatives (NPGs) were prepared by published procedures [10–13] and their electrochemical properties described earlier [14,15].

The dye tested was prepared using methods described elsewhere [16]. The crude dye was purified using column chromatography and finally by a preparative thin layer chromatography. The final product was identified by ^{1}H NMR and ^{13}C NMR spectroscopy. The spectra obtained were evidence that the dye was of the desired structure.

The absorption spectra was obtained using a Varian Cary 3E spectrophotometer. The spectra was obtained in ethyl acetate solution.

The kinetics of free radical polymerization were studied using a polymerization solution composed of 1 ml of MP and 9 ml of TMPTA. The dye concentration was 1×10^{-3} M; concentration of NPG was 0.1 M. As a reference sample identical polymerization solution containing only the dye was used. The concentration of the tested photoinitiator in compositions used for real-time IR measurements were 0.1 M. Before curing, the polymerizing mixture was not deareated.

The kinetics of polymerization were carried out by measuring the polymerization heat evolution of a sample

---

* Corresponding author.

1010-6030/99/$ – see front matter
PII: S1010-6030(99)00158-6

(irradiated with laser beam through an optical system) in a home-made micro-calorimeter [14,17]. The second method, real time IR spectroscopy (RTIR) ([18–20] and references therein), allowed the rate of the monomer double bond disappearance to be monitored in real time. The IR spectrometer (Specord-IR 71, Carl-Zeiss Jena) was set in the transmission mode, and the detection wavelength 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=CH$_2$ twisting). The signal was transformed with an analog/digital data acquisition board to a computer. A thin monomer film (transmitance at 810 cm^{-1} in a range of 90%) was coated onto a polyethylene sheet and placed between NaCl salt discs.

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.

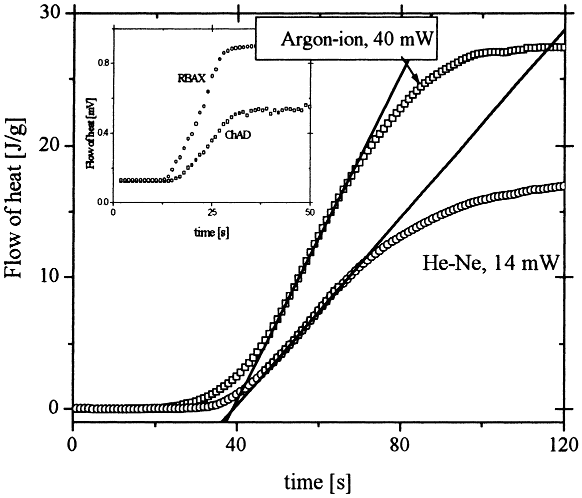
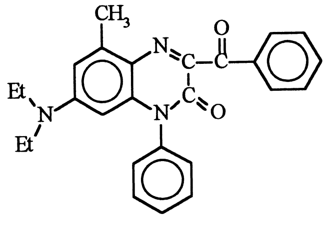


Fig. 1. The flow of heat (thick layer method) during laser initiated polymerization of trimethylolpropane triacrylate–1-methyl-2-pyrrolidinone (TMPTA–MP) mixture. Initiating system ChAD (10^{-3} M) – *N*-phenylglycine (0.1 M). Laser type indicated in figure. Inset: the flow of heat during laser initiated polymerization of TMPTA–MP mixture (9 : 1) initiated by photoredox pair marked in the figure.

3. Results and discussion

Structure of the tested dye, 3-benzoyl-7-diethylamino-5-methyl-1-phenyl-1H-quinoxalin-2-one (**ChAD**), is presented below and its photophysical properties are summarized in Table 1.



ChAD

Fig. 1 shows the examples of the kinetic curves of photopolymerization for **ChAD** initiated both by argon-ion and He–Ne lasers. The sensitivity of the tested dyeing photoinitiator is comparable to the sensitivity of Rose bengal derivative, RBAX, described by Neckers [22] (see Fig. 1, inset).

Since the triplet state of **ChAD** is quenched by the effective electron donor, one might expect that the quenching process occurs via the intermolecular electron transfer process (PET). which allows to calculate the free energy change for the electron transfer process [23,24]. The value of ΔG^0_{ET} can be expected to reflect the trend of change in the efficiency of the electron transfer and for allowed PET reaction its value should be negative. For the tested dye the variations of the driving force of the electron transfer can be introduced by using *N*-phenyglycine derivatives (NPGs) with the oxidation potentials varying from 343 mV (4-OMe-NPG) to 781 mV (4-NO$_2$-NPG) [14]. The rate constant for the quenching of ChAD triplet state by *N*-phenylglycine is equal to 1.2×10^7 M^{-1} s^{-1}, e.g. is three orders of magnitude below the diffusion limit. This creates a unique opportunity to verify the possibility of the use of the Marcus theory [25–27] for prediction of the rate of polymerization or for characterization of the reactivity of free radicals yielded after the photoinduced electron transfer process. Fig. 2 presents examples of the kinetic curves of photopolymerization recorded using RTIR method.

The experimental results presented in Fig. 2 show that the rate of photoinitiated polymerization strongly depends on the type of NPG used. The highest value of the rate is observed for NPGs giving the lowest values of ΔG^0_{ET} and the lowest rate of polymerization is observed for 2-Cl-NPG and 2-NC-NPG which have the value of ΔG^0_{ET} slightly positive. This finding is more precisely illustrated in Fig. 3.

It is clear, from the inspection of the data presented in Fig. 3, that the rate of polymerization initiated by the

Table 1

Absorption; $\lambda_{\max}$ (nm)	$\varepsilon_{\lambda_{\max}}$ (dm^3 cm^{-1} mo1^{-1})	E_{red} (V)	E_{T} (kcal/mol)	$(\Phi_{\mathrm{T}})^{\mathrm{a}}$	τ_{T} (μs)	$(k_q^T)^{\mathrm{b}}$ (M^{-1} s^{-1})	$(\Delta G^0_{\mathrm{ET}})^{\mathrm{c}}$ (kcal/mol)
643	6000	−1.208	44	0.078	25	1.2×10^7	−6.32

[a] Evaluated based on the efficiency of singlet oxygen formation.

[b] *N*-phenylglycine used as the triplet state quencher [21].

[c] Calculated for *N*-phenylglycine as electron donor.

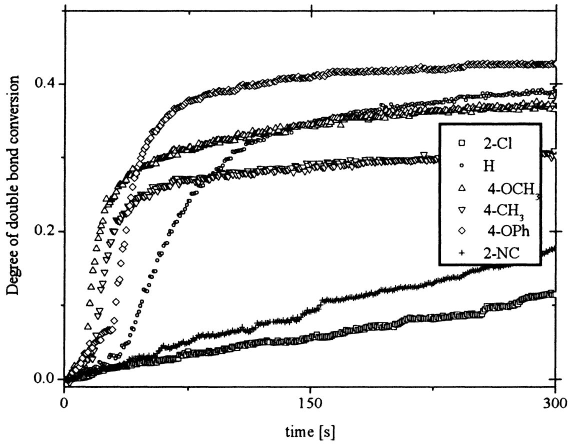


Fig. 2. Rate of vinyl double bond conversion (measured using RTIR methodology) of TMPTA–MP; Initiator: ChAD, electron donor: (1) 2-Cl-NPG, (2) NPG, (3) 4-H$_3$CO-NPG, (4) 4-H$_3$C-NPG, (5) 4-PhO-NPG, (6) 2-NC-NPG.

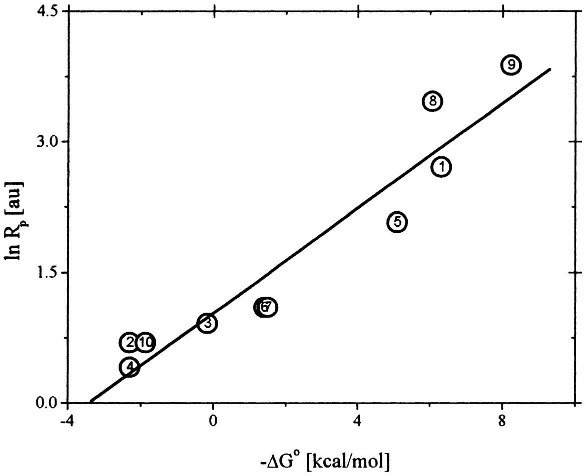


Fig. 3. Relationship between the rate of TMPTA-MP mixture (9 : 1) polymerization and ΔG^0. Photoredox pairs: ChAD-NPGs. *N*-Phenylglycine substituent: (1) H, (2) 3-CN, (3) 4-CN, (4) 2-CN, (5) 4-Cl, (6) 4-C(O)OC$_2$H$_5$, (7) 4-C(O)CH$_3$, (8) 4-CH$_3$, (9) 4-OCH$_3$, (10) 4-NO$_2$.

ChAD-NPGs systems increases when the driving force of electron transfer increases. This behavior is predicted by classical theory of the photoinduced electron transfer [25–27]. On the other hand, the variation in the rate of polymerization can be explained by the different reactivity of the free radicals formed as a result of processes occurring after the electron transfer. Since applied in our study electron donors are aromatic compounds, one can expect that the reactivity of the free radicals can be affected by the type of the substituent. This type of dependence was described by Mateo et al. [28]. These authors have shown that the relative reactivity of radicals derived from dimethylanilines increases as the Hammett parameter σ_{p}, increases. The relationship between the relative rates of polymerization and Hammett constant for ChAD-NPGs tested is presented in Fig. 4.

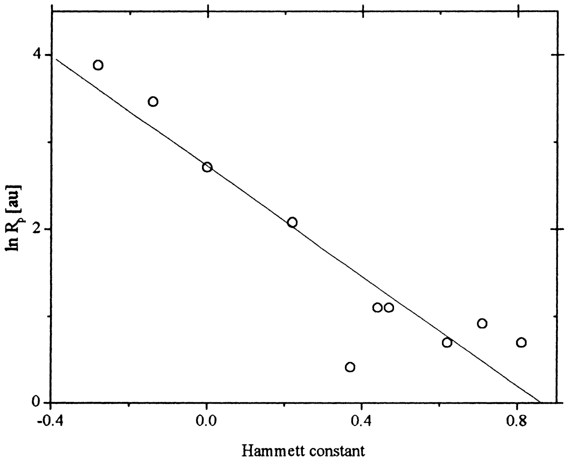


Fig. 4. Relationship between the rate of TMPTA-MP mixture (9 : 1) polymerization and the Hammett constants for NPGs, initiator: ChAD.

From kinetic point of view, a mechanism describing photoinitiated polymerization via PET (not considering kinetic of free radical formation process) process, which contains all major processes can be presented as follows:

$$\mathrm{ChAD} \xrightarrow{h\nu,\mathrm{NPG}} \mathrm{ChADH}^\bullet + \mathrm{NPG}^\bullet \qquad I_a \Phi_{\mathrm{NPG}^\bullet} \tag{1}$$

$$\mathrm{NPG}^\bullet \xrightarrow{k_q} \mathrm{NPG} \qquad k_q[\mathrm{NPG}^\bullet] \tag{2}$$

$$\mathrm{NPG}^\bullet + \mathrm{M} \xrightarrow{k_i} \mathrm{NPGM}^\bullet \qquad k_i[\mathrm{M}][\mathrm{NPG}^\bullet] \tag{3}$$

$$\mathrm{NPG}^\bullet + \mathrm{NPG}^\bullet \xrightarrow{k_r} \mathrm{NPG{-}NPG} \qquad k_r[\mathrm{NPG}^\bullet]^2 \tag{4}$$

$$\mathrm{NPGM}^\bullet + n\mathrm{M} \xrightarrow{k_p} \mathrm{NPG}\dot{\mathrm{M}}_{n+1} \qquad k_p[\mathrm{M}][\mathrm{NPGM}^\bullet] \tag{5}$$

$$\mathrm{NPG}\dot{\mathrm{M}}_{n+1} + \mathrm{NPG}\dot{\mathrm{M}}_{m+1} \xrightarrow{k_t} \mathrm{NPGM}_{n+m+2}$$
$$k_t[\mathrm{NPG}\dot{\mathrm{M}}_{n+1}][\mathrm{NPG}\dot{\mathrm{M}}_{m+1}] \tag{6}$$

The reactivity of free radicals depends on their structure, therefore, in the initiation process of the chain (Eq. (3)) only a part of free radicals efficiently participate. For aromatic radicals one can apply the Hammett equation for the description of initiation rate constant, k_i

$$k_i = \mathrm{e}^{\rho\sigma} \tag{7}$$

and than under steady-state condition

$$\mathrm{e}^{\rho\sigma}[\mathrm{M}][I_a\Phi_{\mathrm{NPG}^\bullet}] = k_t[\mathrm{NPG}\dot{\mathrm{M}}_{n+1}][\mathrm{NPG}\dot{\mathrm{M}}_{m+1}]$$
$$= k_t[\mathrm{NPG}^\bullet]^2 \tag{8}$$

Thus, free radicals concentration is described as follows

$$[\mathrm{NPG}^\bullet] = \left([\Phi_{\mathrm{NPG}^\bullet}]\right)^{0.5}(I_a)^{0.5}[\mathrm{M}]^{0.5}(\mathrm{e}^{\rho\sigma})^{0.5}(k_t)^{-0.5} \tag{9}$$

under this condition the rate of polymerization is

$$R_p = k_p[\mathrm{M}]^{1.5}\left([\Phi_{\mathrm{NPG}^\bullet}]\right)^{0.5}(I_a)^{0.5}(\mathrm{e}^{\rho\sigma})^{0.5}(k_t)^{-0.5} \tag{10}$$

or in logarithmic form

$$\ln R_p = \ln A + 0.5\rho\sigma \tag{11}$$

where A for initial time of polymerization is the sum: $\ln k_p - 0.5\ln k_t + 1.5\ln[\mathrm{M}] + 0.5\ln \Phi_{\mathrm{NPG}\bullet} + 0.5\ln I_a$. Eq. (10) clearly shows that the rate of polymerization depends on the reactivity of free radicals yielded after photoinduced electron transfer process. This is visibly reflected by the data presented in Fig. 4.

4. Conclusions

Tested 3-benzoyl-7-diethylamino-5-methyl-1-phenyl-1H-quinoxalin-2-one, (**ChAD**) is, in the presence of the effective electron donors, a good dyeing initiator of free radical polymerization. Photoinitiation ability strongly depends on the type of *N*-phenylglycine derivative. The results show that the relative rate of polymerization can be described as the linear function of either free energy of activation for the electron transfer process (ΔG^0_{ET}) or linearly depends on the reactivity of the free radicals obtained as a result of secondary processes that are following the electron transfer. It is hard, however, univocally to point out the process which is responsible for these specific behaviors. It is possible that for ChAD-NPGs system, the combination of parameters that are governing the electron transfer process and the reactivity of free radicals are responsible for the observed phenomena. The verification of the polymerization rate limiting parameter (PET process or reactivity of free radicals) is probably possible after the measurements of the rate of the ChAD triplet state quenching by NPGs.

Acknowledgements

This research was sponsored by the State Committee for Scientific Research (KBN), grant No. 3 TO9B 087 15.

References

[1] A.J. Vittum, J. Weissberger, Photogr. Sci. 2 (1954) 81.
[2] G.H. Brown, J. Figureas, R.J. Gledhill, C.J. Kibler, F.C. McCrossen, S.M. Parmerter, P.W. Vittum, A. Weisberger, J. Am. Chem. Soc. 79 (1957) 2919.
[3] G. Tacconi, G. Marinoni, P.P. Righetti, G. Desimoni, J. Prakt. Chem. 322 (1980) 674.
[4] Z. Kucybała, J. Gaca, J. Prakt. Chem. 330 (1988) 435.
[5] W.F. Smith, W.G. Herkstoeter, K.L. Eddy, Photogr. Sci. Eng. 20 (1976) 140.
[6] G.H. Brown, B. Graham, P.W. Vittum, A. Weissberger, J. Am. Chem. Soc. 73 (1951) 913.
[7] E.B. Knott, P.J.S. Pauwels, J. Org. Chem. 33 (1968) 2120.
[8] Z. Kucybała, J. Pączkowski, Polymer 34 (1993) 1558.
[9] Z. Kucybała, M. Pietrzak, J. Pączkowski, Chem. Mater. 10 (1998) 3555.
[10] E. Knoevenagel, Ber. 37 (1904) 4065.
[11] C.G. Schwalbe, W. Schulz, H. Jochheim, Ber. 41 (1908) 3790.
[12] J.E. Trophe, A.S. Wood, J. Chem. Soc. 103 (1913) 1601.
[13] C.A. Bischoff, A. Hausdörfer, Ber. 25 (1892) 2345.
[14] J. Pączkowski, M. Pietrzak, Z. Kucybała, Macromolecules 29 (1996) 5057.
[15] J. Kabatc, Z. Kucybała, M. Pietrzak, F. Scigalski, J. Pączkowski, Polymer 40 (1999) 735.
[16] W.F. Smith, W.G. Herkstroeter, K.L. Eddy, J. Am. Chem. Soc. 97 (1975) 2764.
[17] J. Pączkowski, Z. Kucybała Macromolecules 28 (1995) 269.
[18] C. Decker, K. Moussa, Makromol. Chem. 189 (1988) 2381.
[19] C. Decker, K Moussa, Macomolecules 22 (1989) 4455.
[20] C. Decker, K. Moussa, ACS Symp. Ser. 417 (1990) 439.
[21] Z. Kucybal,a, I. Pyszka, B. Marciniak, G.L. Hug, J. Pączkowski, J. Chem. Soc. Perkin 2, in press.
[22] O. Valdes-Aquilera, C.P. Pathak, J. Shi, D. Watson, D.C. Neckers, Macromolecules 25 (1992) 541.
[23] D. Rehm, A. Weller, Ber. Bunsen-Ges. Phys. Chem. 73 (1969) 834.
[24] D. Rehm, A. Weller, Isr. J. Chem. 8 (1970) 259.
[25] R.A. Marcus, Annu. Rev. Phys. Chem. 15 (1969) 155.
[26] R.A. Marcus, J. Chem. Phys. 67 (1963) 853.
[27] R.A. Marcus, J. Chem. Phys. 43 (1965) 679.
[28] J.L. Mateo, P. Bosh, A.E. Lozano, Macromolecules 27 (1994) 7794.