

Synergetic effects of amines on the intra-ion-pair electron transfer dye photosensitization system $\text{Eo}(\text{IPh}_2)_2$

Jun-Hui He *, Miao-Zhen Li, Jian-Xing Wang, Er-Jian Wang

Institute of Photographic Chemistry, Academia Sinica, Beijing 100101, People's Republic of China

Received 8 November 1994; accepted 21 December 1994

Abstract

Stationary and transient spectroscopic studies on the eosin bis(diphenyliodonium) salt/triethylamine ($\text{Eo}(\text{IPh}_2)_2/\text{TEA}$) system were carried out in comparison with $\text{Eo}(\text{IPh}_2)_2$ alone. In non-polar solvents where $\text{Eo}(\text{IPh}_2)_2$ forms contact ion pairs, TEA molecules insert themselves between the anions and cations, resulting in the formation of amine-separated ion pairs. When exposed to visible light, $\text{Eo}(\text{IPh}_2)_2/\text{TEA}$ undergoes oxidative electron transfer firstly. Synergetic effects of amines on $\text{Eo}(\text{IPh}_2)_2$ were found for which a cyclic regenerative mechanism was proposed. $\text{Eo}(\text{IPh}_2)_2/\text{TEA}$ was applicable for various monomers and unsaturated oligomers, especially of the acrylate type, even in the presence of oxygen. Concentration effects of $\text{Eo}(\text{IPh}_2)_2$, amine and monomer were also investigated.

Keywords: Synergetic effects; Ion pair; Electron transfer; Dye photosensitization; Iodonium salt

1. Introduction

Most photopolymerizable compositions used at the present time are sensitive only to UV light. Recently a number of new and promising techniques, including laser-induced photocuring, have been developed. In these techniques, visible or near-IR sensitivity is required by light-emitting diodes or laser diodes. Efforts to extend the photoresponse of useful photoinitiators for free-radical polymerization to the visible region have up to now met with only modest success. For these reasons, dye sensitization systems have attracted much attention again [1], because a large variety of commercial dyes over the entire visible and near-IR region can be chosen as desired. In general, photosensitization is a bimolecular energy or electron transfer process. In highly viscous and rigid polymeric reaction systems it is difficult to achieve efficiently on such a short time scale of excited state lifetimes, since the molecular mobility is very low. In recent years a number of new photosensitization systems have been reported where the sensitizer is bonded to the reactant by chemical methods that facilitate ion pair formation and shows much higher efficiency through intramolecular energy or electron transfer, especially in highly viscous and rigid polymeric systems [2–4]. One such system is eosin bis(diphenyliodonium) salt ($\text{Eo}(\text{IPh}_2)_2$). In media of vari-

ous polarities it exists in such different forms as contact ion pairs, solvent-separated ion pairs, solvated free ions or mixtures thereof [5]. It is stable in the dark and undergoes fast electron transfer when exposed to visible light, resulting in fast bleaching of the dye anion. With very high extinction coefficients, such types of photoinitiator have to be used in low concentrations owing to the light-screening effect. Therefore it is highly desirable that the dye anion be recycled to maintain its concentration and thus to keep the reaction rate high. The active radicals formed can initiate polymerization of vinyl monomers or cross-linking of unsaturated resins. Tertiary amines (TA) were reported to be activators for fluorescein derivatives (FD) [1] and to be able to form charge transfer complexes with onium salts (On^+X^-) which shift the absorption from below 300 nm to the visible region [6]. The two systems, FD/TA and $\text{On}^+\text{X}^-/\text{TA}$ are both photoinitiators for radical polymerization. Tertiary amines such as *N,N*-dialkylaniline and *N,N,N',N'*-tetraalkylphenylenediamine are also well known auto-oxidants. In this work the effects of amines on the $\text{Eo}(\text{IPh}_2)_2$ type of photoinitiator were estimated.

2. Experimental details

Eosin bis(diphenyliodonium) salt was synthesized as previously described [3].

* Corresponding author.

Methyl methacrylate, styrene and acrylonitrile were purified according to conventional methods and distilled before use. Other reagents were all analytical grade and used as purchased.

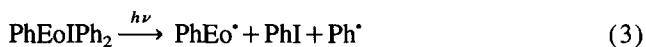
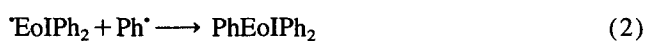
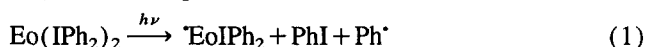
UV–visible absorption and fluorescence emission spectra were recorded on a Hitachi 557 UV–visible spectrophotometer and a Hitachi MPF-4 fluorimeter. Transient absorption spectra were obtained with a nanosecond laser flash photolysis apparatus utilizing a pulsed laser of 532 nm wavelength. The light source for photopolymerization was a 400 W xenon lamp, the UV light (less than 300 nm) from which was filtered off by thick Pyrex glass. The light intensity reaching samples was 15.95 mW cm^{-2} . Polymerization rates were measured with Pyrex dilatometers (diameter 10 mm) which rotated around the light source at $8\text{--}9 \text{ rev min}^{-1}$ on a merry-go-round in a thermostatted photoreaction bath (30°C). The experimental data were treated by a least-squares method.

3. Results and discussion

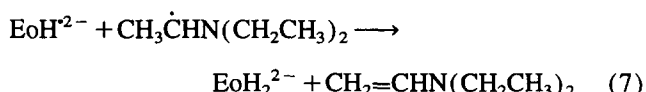
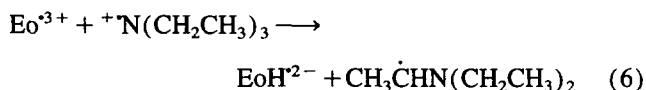
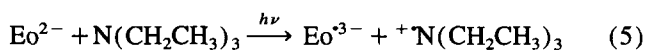
3.1. Photochemical processes of $\text{Eo}(\text{IPh}_2)_2/\text{triethylamine}$ (TEA)

$\text{Eo}(\text{IPh}_2)_2$, eosin (EoNa_2)/TEA and diphenyliodonium chloride (Ph_2ICl)/TEA have all been reported to be photoinitiators for free-radical polymerization. When exposed to visible light, they undergo the following reactions (a), (b) and (c) respectively.

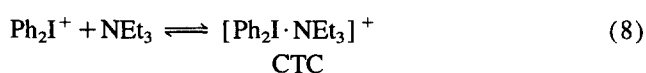
(a) Intra-ion-pair oxidative electron transfer:



(b) Reductive electron transfer:



(c) Electron transfer through a charge transfer complex (CTC):



As described in Refs. [5,7], the above three systems have different spectroscopic characteristics. $\text{Eo}(\text{IPh}_2)_2$ exists only as contact ion pairs which show a characteristic set of absorp-

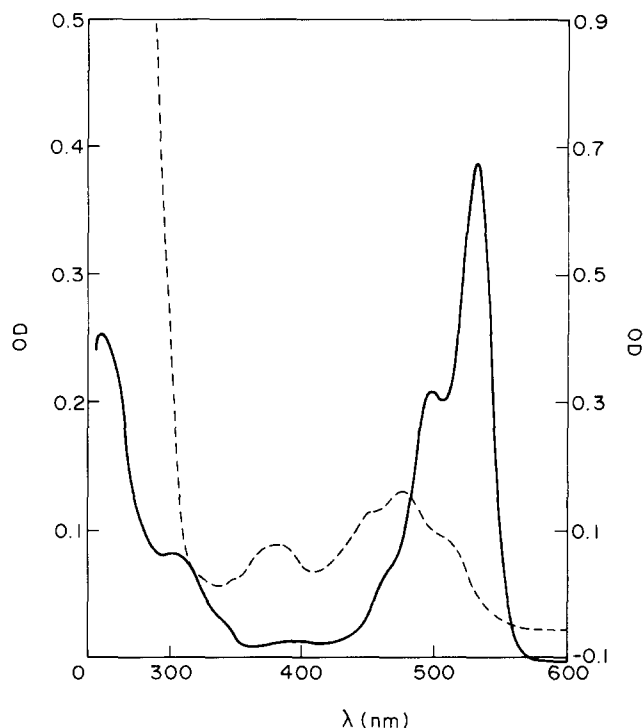


Fig. 1. Absorption spectra of $\text{Eo}(\text{IPh}_2)_2/\text{TEA}$ (—) and $\text{Eo}(\text{IPh}_2)_2$ (---) in 1,4-dioxane ($[\text{Eo}(\text{IPh}_2)_2] = 1.00 \times 10^{-5} \text{ M}$, $[\text{TEA}] = 2.51 \times 10^{-2} \text{ M}$, presence of nitrogen).

tion bands at 380 and 445 nm in non-polar solvents. With increasing solvent polarity, the contact ion pairs dissociate into solvent-separated ion pairs or solvated free ions, both of which have a characteristic set of absorption bands at 500 and 532 nm. The charge transfer complex formed from Ph_2ICl with TEA shows a strong, wide absorption band at 507 nm, the tail of which extends up to 700 nm. In contrast, addition of TEA to the eosin solution does not result in any spectral change.

For the $\text{Eo}(\text{IPh}_2)_2/\text{TEA}$ system it seemed that the above reactions (a), (b) and (c) would all occur under visible light irradiation.

In Fig. 1 the absorption spectra of $\text{Eo}(\text{IPh}_2)_2$ and $\text{Eo}(\text{IPh}_2)_2/\text{TEA}$ in the non-polar solvent 1,4-dioxane are compared. No characteristic absorption band was observed for the above charge transfer complex in the spectrum of $\text{Eo}(\text{IPh}_2)_2/\text{TEA}$, indicating that iodonium ions have no interaction or at most a weak interaction with amines in this case. Nevertheless, it is noted that $\text{Eo}(\text{IPh}_2)_2$ in 1,4-dioxane has the characteristic set of absorption bands of contact ion pairs, while $\text{Eo}(\text{IPh}_2)_2/\text{TEA}$ shows a characteristic set of absorption bands like those of solvent-separated ion pairs or solvated free ions. The polarity of TEA ($E_T(30) = 32.1$) is smaller than that of 1,4-dioxane ($E_T(30) = 36.0$), so the above spectral difference is unlikely to result from an increase in medium polarity as usually reported before [5,7]. It is thought that TEA molecules may have a weak interaction with iodonium ions and thus insert themselves between eosin anions and iodonium cations of contact ion pairs, resulting in the for-

Table 1
Rate constants of fluorescence quenching by DPIOC and TEA in ethanol

Quencher	k_q ($M^{-1} s^{-1}$)
DPIOC	6.03×10^{11}
TEA	1.98×10^8

mation of amine-separated ion pairs which have the same absorption spectrum as the solvent-separated ones.

From the above discussion, the charge transfer complex in Eq. (8) makes no contribution to the visible absorption of $Eo(IPh_2)_2/TEA$. Therefore $Eo(IPh_2)_2/TEA$ does not generate free radicals for polymerization through the CTC when exposed to visible light. To evaluate the relative contributions of intra-ion-pair oxidative electron transfer and reductive electron transfer, fluorescence quenching of $EoNa_2$ by Ph_2ICl and TEA was carried out. As seen in Table 1, the quenching constant for Ph_2ICl is nearly four magnitudes higher than that for TEA. This means that in the $Eo(IPh_2)_2/TEA$ system the intra-ion-pair oxidative electron transfer plays an overwhelming role. Zwicker et al. [8] and Ohno et al. [9] previously reported the transient absorption spectra of eosin cation and anion radicals resulting from eosin losing and obtaining an electron respectively as follows:

$$\lambda_{max}((EoNa_2)^{+\cdot}) = 460 \text{ nm}, \quad \lambda_{max}((EoNa_2)^{-\cdot}) = 410 \text{ nm}$$

Laser flash photolysis results showed the non-existence of the absorption of the anion radical $[Eo(IPh_2)_2]^{-\cdot}$, indicating that the reductive electron transfer was quite slow or did not occur at all.

Active free radicals are able to initiate polymerization of vinyl monomers. Therefore vinyl monomers can be used as radical traps to evaluate the efficiency of radical generation of photoinitiators. For a particular monomer, the higher the polymerization rate, the higher are the photoinitiation efficiency and the efficiency of radical generation. As described later, addition of TEA to the $Eo(IPh_2)_2$ system increases the photoinitiation efficiency of $Eo(IPh_2)_2$. The photobleaching study, however, showed that the photobleaching rate of $Eo(IPh_2)_2/TEA$ is much lower than that of $Eo(IPh_2)_2$ alone (Fig. 2). This is quite interesting, because usually the larger the photobleaching rate, the more radicals the reaction can produce. Another interesting observation is that 50 ns after the above two systems were excited by the 532 nm pulsed laser in acetonitrile solution, the absorption of the eosin iodonium radical (450 nm) was still significant for $Eo(IPh_2)_2$ but almost disappeared for $Eo(IPh_2)_2/TEA$ (Fig. 3). This indicates that eosin iodonium radicals have more ways to decay in $Eo(IPh_2)_2/TEA$ than in $Eo(IPh_2)_2$ alone. The above phenomena are assumed to be attributable to the reduction of eosin iodonium radicals by TEA to the original dye anions [10] (Scheme 1).

The reaction cycle of Scheme 1 on one hand decreases the exhaustion of absorbing species of $Eo(IPh_2)_2/TEA$, thus increasing the overall absorption of visible light by

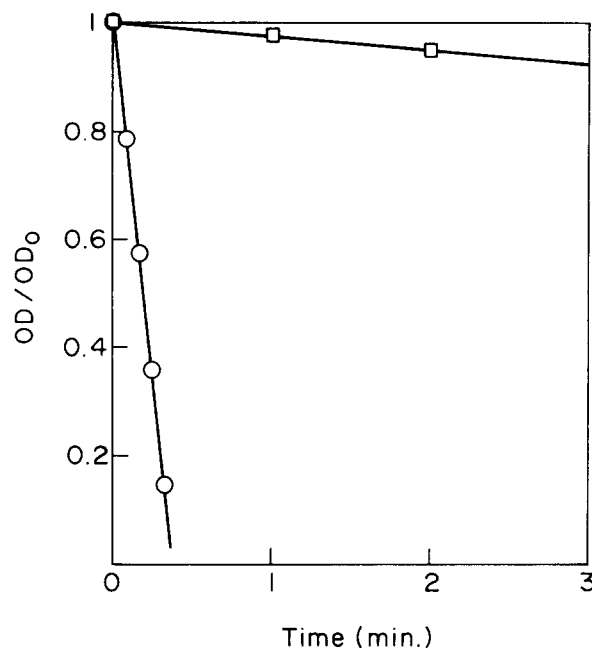


Fig. 2. Photobleaching of $Eo(IPh_2)_2/TEA$ (□) and $Eo(IPh_2)_2$ (○) in 1,4-dioxane ($[Eo(IPh_2)_2] = 1.00 \times 10^{-5} M$, $[TEA] = 2.51 \times 10^{-2} M$, presence of nitrogen).

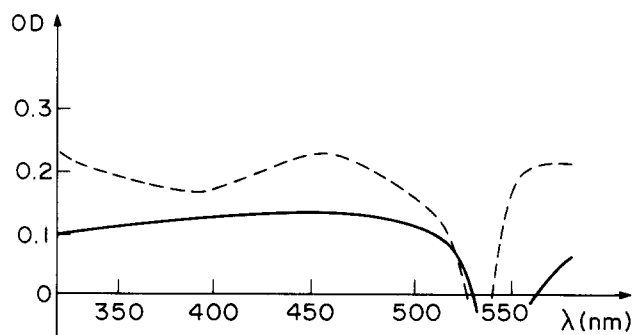


Fig. 3. Transient absorption spectra of $Eo(IPh_2)_2/TEA$ (—) and $Eo(IPh_2)_2$ (---) 50 ns after 532 nm pulsed laser excitation in acetonitrile ($[Eo(IPh_2)_2] = 1.00 \times 10^{-5} M$, $[TEA] = 2.51 \times 10^{-2} M$, presence of nitrogen).

$Eo(IPh_2)_2/TEA$ compared with $Eo(IPh_2)_2$ alone; on the other hand it produces the initiating TEA cation radicals **1** and TEA radicals **2** instead of terminating the eosin radical species. All these effects possibly make the photoinitiation efficiency of $Eo(IPh_2)_2/TEA$ higher than that of $Eo(IPh_2)_2$ alone.

3.2. Polymerization using $Eo(IPh_2)_2/TEA$ as photoinitiator

When exposed to visible light, $Eo(IPh_2)_2/TEA$ can generate active radicals and is thus able to initiate polymerization of vinyl monomers and cross-linking of unsaturated resins. In Fig. 4, polymerizations with $Eo(IPh_2)_2/TEA$ and $Eo(IPh_2)_2$ alone as photoinitiator are compared. The results show a significant synergistic effect of TEA on $Eo(IPh_2)_2$. This is attributed to the cyclic regenerative mechanism proposed in Scheme 1.

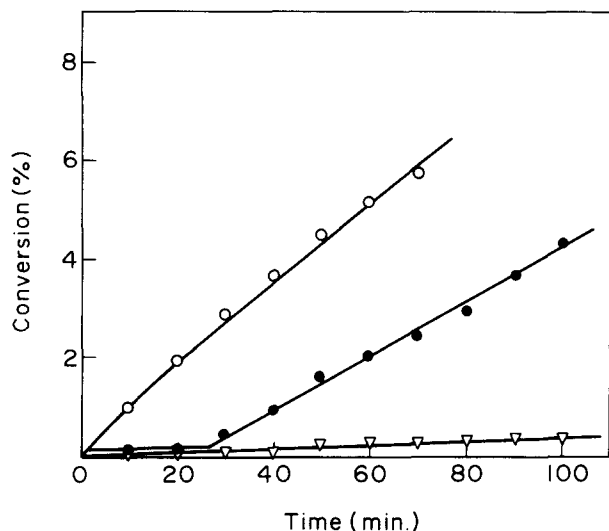


Fig. 6. Effects of oxygen on polymerization of MMA in 1,4-dioxane with Eo(IPh₂)₂/TEA as photoinitiator in the presence of nitrogen (○) and oxygen (●) and with Eo(IPh₂)₂ as photoinitiator in the presence of oxygen (∇) ([Eo(IPh₂)₂] = 5.00 × 10⁻⁴ M, [TEA] = 3.00 × 10⁻² M, [MMA] = 3.76 M).

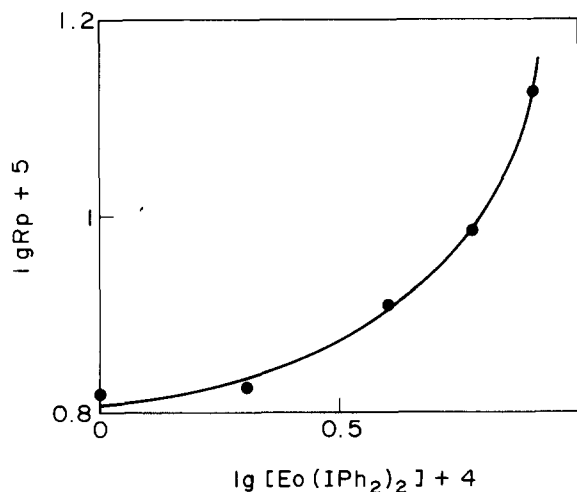


Fig. 7. Effect of [Eo(IPh₂)₂] on polymerization rate in 1,4-dioxane ([TEA] = 3.00 × 10⁻² M, [MMA] = 3.76 M, presence of nitrogen).

unlike the usual cases in which the polymerization rate is directly proportional to a particular power of the initiator concentration, the exponent here is not a constant, i.e. $R_p \propto [Eo(IPh_2)_2]^x$ where x increases with the concentration. This can be once again attributed to the cyclic regenerative mechanism, since with an increase in [Eo(IPh₂)₂], reduction of eosin iodonium radicals by TEA becomes more and more significant. The polymerization rate also increases as [TEA] increases, but R_p is directly proportional to the 0.34 power of [TEA] in the low concentration range and deviates from linear to drop in the high concentration range. As shown in Fig. 9, the polymerization rate increases linearly with increasing monomer concentration. A previous study indicated that addition of acrylate monomers can make the medium polarity higher [11]. This has negative effects on the efficiency of

photogeneration of active free radicals and thus results in deviation of R_p from linear at high monomer concentration. From the above discussion, the following kinetic equation can be proposed:

$$R_p = k[Eo(IPh_2)_2]^x[TEA]^{0.34}[MMA]$$

where [TEA] ≤ 3.00 × 10⁻² mol l⁻¹ and [MMA] ≤ 4.69 mol l⁻¹.

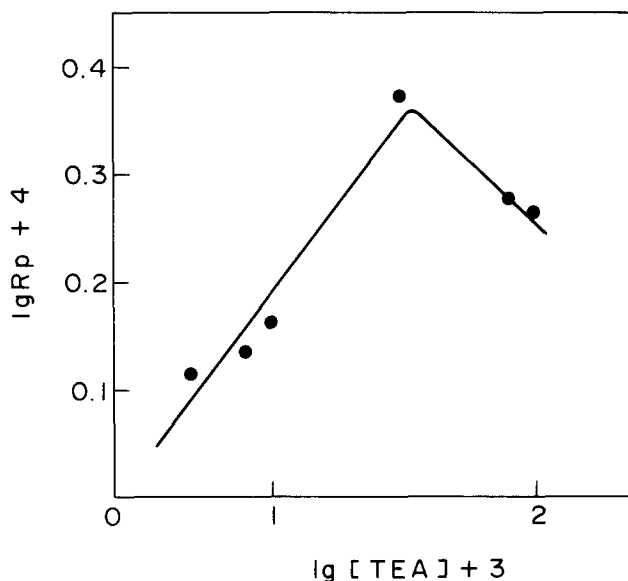


Fig. 8. Effect of [TEA] on polymerization rate in 1,4-dioxane ([Eo(IPh₂)₂] = 5.00 × 10⁻⁴ M, [MMA] = 3.76 M, presence of nitrogen).

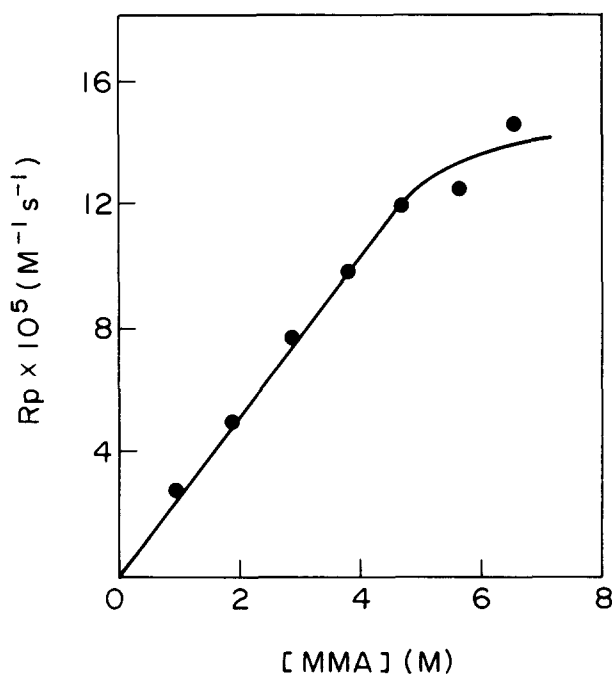


Fig. 9. Effect of [MMA] on polymerization rate in 1,4-dioxane ([Eo(IPh₂)₂] = 5.00 × 10⁻⁴ M, [TEA] = 3.00 × 10⁻² M, presence of nitrogen).

4. Conclusions

Amines are important additives when Eo(IPh₂)₂-type photoinitiators are used in radical polymerization and cross-linking. On one hand they play the role of auto-oxidizers; on the other hand they synergize with the photoinitiators. The latter are associated with recovery of dye dianions and formation of active species according to the cyclic regenerative mechanism of Scheme 1.

Acknowledgement

One of the authors (J.-H.H.) thanks the Foundation of the Chinese Academy of Sciences for Overseas Chinese Scholars for financial support.

References

- [1] D.F. Eaton, in D.H. Volman, K. Gollnick and G.S. Hammond (eds.), *Advances in Photochemistry*, Wiley, New York, 1986, p. 427.
- [2] X.Y. Hong and S.P. Pappas, *Photogr. Sci. Photochem.*, 11 (1993) 256.
- [3] J.H. He and E.J. Wang, *Acta Polym. Sinica*, (4) (1992) 564.
- [4] Z.Y. Chang, J.H. He, M.Z. Li and E.J. Wang, *Chinese J. Appl. Chem.*, 10 (1993) 47.
- [5] J.H. He, W.H. Zhou, H.M. Chen, E.J. Wang, N.S. Allen and M. Derham, *Acta Chim. Sinica*, in press.
- [6] J.H. He and E.J. Wang, *Chinese J. Polym. Sci.*, 8 (1990) 36.
- [7] W.H. Zhou, J.H. He, M.Z. Li and E.J. Wang, *Photogr. Sci. Photochem.*, in press.
- [8] E.F. Zwicker and L.I. Grossweiner, *J. Phys. Chem.*, 67 (1963) 549.
- [9] T. Ohno, S. Kaio and M. Koizumi, *Bull. Chem. Soc. Jpn.*, 29 (1966) 232.
- [10] T. Shen, Z.G. Zhao, Q. Yu and H.J. Xu, *J. Photochem. Photobiol. A: Chem.*, 47 (1989) 203.
- [11] J.H. He, M. Li, J.X. Wang, E.J. Wang, N.S. Allen and M. Derham, *Acta Polym. Sinica*, in press.