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Sensitized photolysis of diphenyliodonium through intra-ion-pair electron transfer — a novel near-UV photoinitiator: diphenyliodonium 9-anthroate

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Abstract

A novel near-UV photoinitiator, diphenyliodonium 9-anthroate, was synthesized by metathesis, characterized and studied. In media of different polarity, this compound shows similar absorption properties, but very different fluorescence and photochemical properties. When irradiated with near-UV light, the anion absorbs radiation and induces electron transfer to iodonium ion. The active free radicals thus formed initiate the polymerization of methyl methacrylate. © 1997 Elsevier Science S.A.

Keywords: Electron transfer; Iodonium salt; Ion-pair; Photoinitiator; Photosensitization

1. Introduction

Iodonium and sulphonium salts are newly developed photoinitiators for both cationic and radical polymerization [1–3]. Unfortunately, most have absorption maxima below 300 nm, with little or no photoactivity at wavelengths above the glass cut-off point. Because their absorptivity above 300 nm is very low, they do not match many important light sources, including the He–Cd laser which has an emission at 325 nm, and their applications are relatively limited. To extend their absorptivity above 300 nm, the sensitization of iodonium and sulphonium salts has been extensively investigated [4,5]. For example, anthracene has a large molar extinction coefficient near 325 nm (approximately 10^4 $\mathrm{mol^{-1}\,l\,cm^{-1}}$) and a large free energy of photoinduced electron transfer with onium salts; therefore it is a very good photosensitizer for onium salts [6]. Nevertheless, in most cases, the photosensitization occurs through an intermolecular electron transfer mechanism, the efficiency of which is restricted by diffusion. In highly viscous and rigid polymeric reaction systems, this phenomenon is quite significant. In recent years, work from several laboratories has revealed that ion-pairing and chemical bonding of the sensitizer and onium salt can eliminate the limitation imposed by diffusion [7,8]. More recently, a binary system, 9-anthroic acid–diphenyliodonium chloride (AA–DPIOC), has been studied in our laboratory. The large negative value of the free energy of electron transfer ΔG (-2.07 eV) calculated by the Rehm–Weller equation indicates that an electron transfer mechanism is feasible for the sensitized photolysis of DPIOC by AA through its excited singlet state. The fluorescence quenching rate constant K_q of AA by DPIOC (8.6×10^{10} $\mathrm{l\,mol^{-1}\,s^{-1}}$) is much greater than the bimolecular diffusion rate constant, which shows that it results at least partially from intra-ion-pair reaction. Gas chromatography–mass spectrometry (GC–MS) and photochemically induced dynamic nuclear polarization (photo-CIDNP) results obtained with AA–DPIOC after exposure to radiation indicated that electron transfer occurs to produce a singlet radical pair which can further produce cage escape products (such as benzene). Alternatively, intersystem crossing, resulting in a triplet radical pair from which back electron transfer takes place, can occur.

In this work, a novel ion-pair compound of diphenyliodonium 9-anthroate (DPIOA) was synthesized and studied with regard to its photophysical and photochemical properties and photoinitiation ability for radical polymerization.

2. Experimental details

2.1. Synthesis of DPIOA

The synthesis of DPIOA was carried out as shown in Scheme 1. Thus aqueous solutions of 17.8 g of $AgNO_3$ and 4.4 g of NaOH were mixed. A dark brown Ag_2O precipitate appeared immediately. On standing for a while, it was isolated

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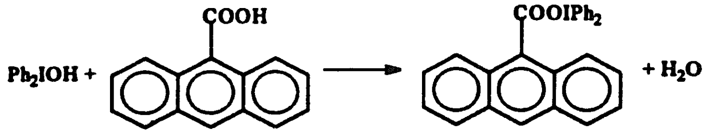
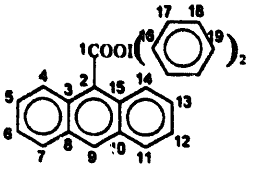
$$AgNO_3 + NaOH \longrightarrow Ag_2O + H_2O + NaNO_3$$

$$Ag_2O + Ph_2ICl + H_2O \longrightarrow Ph_2IOH + AgCl$$



Scheme 1.

by filtration and washed three times with distilled water. DPIOC (9.2 g) was ground with the above Ag_2O and a little distilled water for 1 h in a glass mortar with a pestle. The slurry was filtered through a sintered glass filter and washed six times with distilled water. The filtrate was collected in a 1000 ml Erlenmeyer flask into which 4.0 g of AA was added. After stirring, a pale yellow precipitate was obtained. The precipitate was isolated by filtration and washed with distilled water until the filtrate became neutral. The solid was then dissolved in boiled acetonitrile and the hot solution was filtered immediately to remove insoluble material. On standing, a pale yellow crystal was obtained. After filtration, the crystal was washed twice with acetonitrile and dried in vacuum. The yield and melting point of the product DPIOA were 52% and 105–107 °C respectively. Thin layer chromatography (TLC) with ethanol as the solvent and 60% methanol–40% acetone as the developer showed a single spot, indicating the high purity of the product. IR (KBr disc): 3044 cm^{-1}, 2931 cm^{-1} (m, Ar–H), 1539 cm^{-1} (vs, COO^-, asymmetric), 1467 cm^{-1} (m, COO^-, symmetric), 990 cm^{-1} (s, C–I), 733 cm^{-1} (s, monosubstitution in benzene ring), no more 1673 cm^{-1} (vs, C=O (COOH)). ^{13}C NMR (CD_3OD): 177.707 ppm (w, C-1), 136.281 ppm (s, C-19), 133.470 ppm (s, C-18), 133.059 ppm (s, C-17), 116.355 ppm (w, C-16), 126.273 ppm (s, C-5, C-6, C-12, C-13), 126.337 ppm (s, C-9), 127.890 ppm (s, C-4, C-7, C-11, C-14), 129.251 ppm (s, C-2), 132.994 ppm (w, C-3, C-8, C-10, C-15).



Methyl methacrylate (MMA) was purified according to a conventional method and distilled before use. Other reagents were all of analytical grade and were used as purchased.

UV absorption and fluorescence emission spectra were recorded on a Hitachi 557 UV–visible spectrophotometer and a Hitachi MPF-4 fluorometer respectively. The photoreaction was carried out using a 300 W high pressure mercury lamp. The incident light was passed through a piece of Pyrex glass before reaching the cell containing DPIOA solution. The light intensity was measured to be 1.3 mW cm^{-2} by a Blak-Ray ultraviolet meter. The light source for photopolymerization was a 375 W high pressure mercury lamp; UV light of less than 300 nm was filtered off by thick Pyrex glass. The light intensity reaching the sample was determined using the benzophenone/benzophenol actinometer to be 2.2×10^{16} photons min^{-1} cm^{-2}. Polymerization rates were measured with Pyrex dilatometers (diameter, 10 mm) which rotated around the light source at 8–9 rev min^{-1} on a merry-go-round in a thermostatically controlled photoreaction bath (30 °C). The experimental data were treated by a least-squares method.

3. Results and discussion

3.1. UV absorption and fluorescence spectra and their solvent effects

$E_T(30)$ is an important parameter for measuring the solvent polarity. The larger the $E_T(30)$ value, the more polar the solvent. The $E_T(30)$ values of various solvents can be obtained from the literature [9]. Various solvents, whose $E_T(30)$ values cover the range 36.0–55.4, were selected to study the photophysical and photochemical properties of DPIOA. The UV absorption and fluorescence data are shown in Tables 1 and 2 respectively. The solvent polarity has little influence on the UV absorption properties of DPIOA. Nevertheless, it has a significant effect on the fluorescence properties of DPIOA. In solvents of low polarity, a single broad fluorescence peak is observed. In solvents of higher polarity,

Table 1
UV absorption data of DPIOA in various solvents of different polarity

Solvent	$E_T(30)$	λ_{max} (nm) ($\varepsilon_{max} \times 10^3$ ($mol^{-1}\,l\,cm^{-1}$))				
1,4-Dioxan	36.0	316 (1.58)	334 (3.03)	348 (5.41)	365 (7.80)	385 (6.72)
Dimethoxyethane	38.2	315 (2.26)	334 (4.19)	350 (7.79)	367 (11.6)	387 (10.2)
Dichloromethane	40.7	317 (2.38)	334 (4.05)	350 (7.70)	368 (12.1)	389 (11.2)
N,*N*-Dimethylformamide	43.8	317 (1.81)	334 (3.23)	350 (6.35)	368 (9.74)	388 (8.99)
Acetonitrile	45.6	316 (1.34)	331 (2.71)	348 (5.45)	365 (8.46)	385 (7.59)
Ethanol	51.9	316 (1.40)	330 (3.05)	347 (6.08)	364 (9.55)	385 (8.92)
Methanol	55.4	314 (1.40)	330 (3.03)	346 (6.10)	363 (9.45)	383 (8.85)

Table 2
Fluorescence data of DPIOA in various solvents of different polarity [a]

Solvent	$E_T(30)$	λ_{max} (nm)
1,4-Dioxan	36.0	455
Dimethoxyethane	38.2	453
Dichloromethane	40.7	468
N,N-Dimethylformamide	43.8	397(s) [b], 414, 436(s) [b]
Acetonitrile	45.6	397, 415, 435(s) [b]
Ethanol	51.9	392, 410, 434
Methanol	55.4	391, 409, 432

[a] λ_{max} = 320 nm.
[b] s, shoulder.

three relatively sharp fluorescence peaks are observed, the middle peak being the strongest. They are blue shifted with an increase in the solvent polarity. The ion-pair compound DPIOA may exist in the solvent as contact ion-pairs, solvent-separated ion-pairs or solvated free ions. Solvent-separated ion-pairs and solvated free ions have similar spectroscopic properties. Contact ion-pairs, however, usually show different spectroscopic properties from solvent-separated ion-pairs. This is because, in contact ion-pairs, the cation and anion are sufficiently close for their electronic clouds to interact with each other. In contrast, in solvent-separated ion-pairs and solvated ions, the cation and anion do not interact [10]. The coulombic force between the cation and anion is inversely proportional to the dielectric constant of the solvent used, i.e. the smaller the dielectric constant, the larger the coulombic force. Therefore a decrease in the dielectric constant of the solvent forces the cation and anion to become closer [10]. The above changes in the fluorescence spectra may be attributed to the shift of the equilibrium of different species and the stabilization of the ground state of ionic DPIOA with an increase in the solvent polarity.

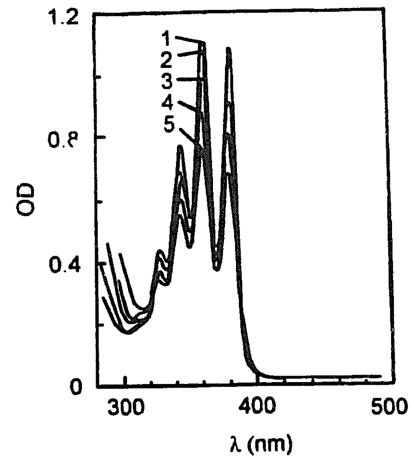


Fig. 1. Absorption spectra of DPIOA in methanol on exposure to UV radiation for times (min): 0 (1); 3.04 (2); 8.01 (3); 18.03 (4); 33.02 (5) ([DPIOA] = 1.1×10^{-4} M, presence of nitrogen).

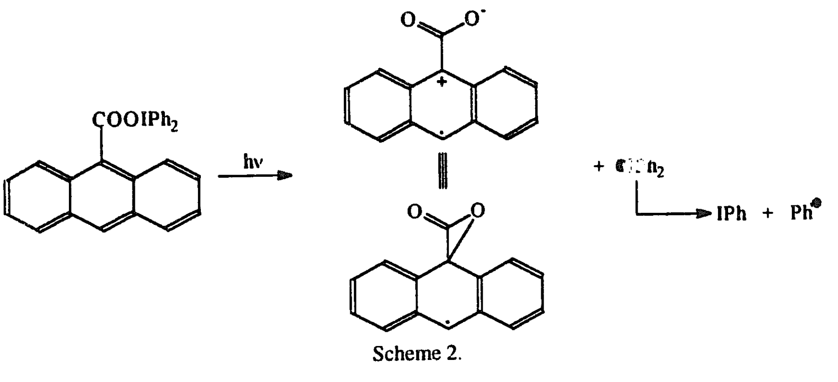
3.2. Photoreaction of DPIOA in various solvents

When exposed to UV radiation, DPIOA undergoes a photoreaction which can be visualized and monitored by UV absorption spectroscopy. One example is shown in Fig. 1. In methanol, the absorption maxima decrease with increasing irradiation time. This is attributed to photoinduced electron transfer between the cation and the anion (Scheme 2).

From Fig. 1, a curve $(OD_0 - OD_t)/OD_0$ vs. t was obtained where OD_0 is the optical density before irradiation and OD_t is the optical density at irradiation time t. The slope of the straight portion of the curve was calculated by a least-squares method and used to describe the photoreaction rate of DPIOA (R). Fig. 2 shows the influence of the solvent polarity ($E_T(30)$) on the photoreaction rate. With a decrease in the solvent polarity, the photoreaction rate increases. This may be caused by the following facts. Firstly, in solvents of low polarity, the cation and anion are much closer than in polar solvents. This results in a larger collision probability, and therefore a larger photoreaction rate. Secondly, the overall charge change is more favourable in solvents of low polarity. After electron transfer, the coulombic attraction no longer exists. The remaining repulsion causes a rapid separation of the formed radical pairs. Finally, diphenyliodine radicals decompose easily, inhibiting back electron transfer.

3.3. Polymerization using DPIOA as photoinitiator

When exposed to UV light, DPIOA can generate active radicals and can initiate the polymerization of vinyl monomers and the cross-linking of unsaturated resins. Fig. 3 shows the results of the polymerization of MMA in the non-polar solvent 1,4-dioxan and the polar solvent acetonitrile. The polymerization rate in 1,4-dioxan is around four times that in acetonitrile. This is attributed to the larger photoreaction rate



Scheme 2.

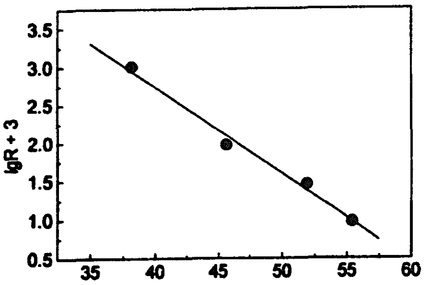


Fig. 2. Effect of solvent polarity ($E_T(30)$) on the photoreaction rate R ([DPIOA] = 1.1×10^{-4} M, presence of nitrogen).

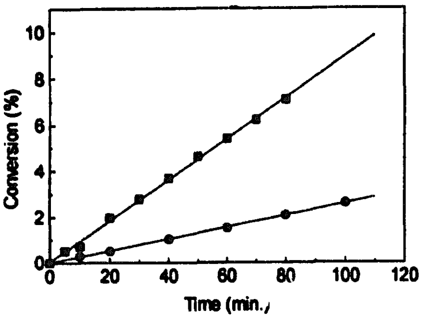


Fig. 3. Percentage conversion vs. time of the polymerization of MMA in 1,4-dioxan (■) and acetonitrile (●) ([DPIOA] = 7.50×10^{-5} M, [MMA] = 2.82 M, presence of nitrogen).

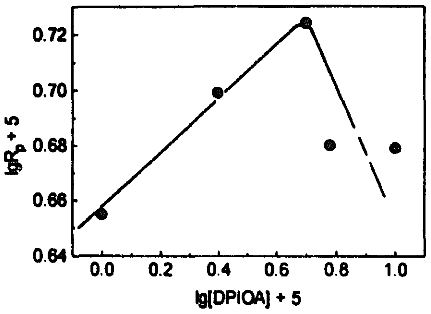


Fig. 4. Effect of [DPIOA] on the polymerization rate of MMA in 1,4-dioxan ([MMA] = 2.82 M, presence of nitrogen).

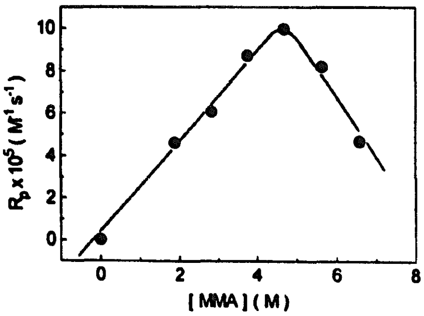


Fig. 5. Effect of [MMA] on the polymerization rate in 1,4-dioxan with DPIOA as photoinitiator ([DPIOA] = 6.00×10^{-5} M, presence of nitrogen).

for the production of active radicals in 1,4-dioxan than in acetonitrile. The effects of the concentration of the photoinitiator and monomer were studied in a nitrogen atmosphere. The results are shown in Figs. 4 and 5. The polymerization rate increases with increasing DPIOA concentration in the low concentration range, but deviates from linearity and decreases in the high concentration range. The deviation in the high concentration range may result from the so-called internal screening effect which causes an inhomogeneous distribution of the absorbed dose, thus forming a high local concentration of excited species and intermediates in the surface region. This, in turn, leads to the rapid initial deactivation of both excited species and intermediates. As shown in Fig. 5, the polymerization rate increases linearly with increasing monomer concentration. A previous study has indicated that the addition of acrylate monomer makes the medium polarity higher [11]. This has a negative effect on the efficiency of photogeneration of active free radicals and thus results in a deviation of R_p from linearity at high monomer concentration.

4. Conclusions

The absorption of iodoniums can be easily red shifted as desired into the near-UV region by the formation of an intra-ion-pair compound of iodonium and the sensitizer anion via metathesis. When exposed to near-UV radiation, the anion is excited to its excited state. Within the lifetime of the excited state, electron transfer from the anion to the cation occurs, producing initiating free radicals for polymerization. Any factor which influences the nature and formation of the ion-pairs will influence the rate and efficiency of intra-ion-pair electron transfer, and thus polymerization.

Acknowledgements

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