

# Photopolymerization of Acrylamide Initiated by the Three-Component System Safranin/Triethanolamine/Diphenyliodonium Chloride: The Effect of the Aggregation of the Salt

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**ABSTRACT:** The effects of diphenyliodonium chloride (DPI) on the polymerization of acrylamide photoinitiated by the dye safranin with triethanolamine as a coinitiator were investigated in aqueous solutions. The salt notably increased the polymerization rate. This accelerating effects increased appreciably at concentrations of DPI at which the light scattering of the solutions became important. The effects of DPI on the photophysical properties of the dye were also investigated. Although the absorption and fluorescence were scarcely affected, the triplet yield increased by 60%. However, the polymerization rate increased by a factor much higher than that of the triplet yield. The results obtained at high concentrations of the salt could be ascribed to the presence of aggregates of the hydrophobic cations. The lower limit established for the formation of the aggregates was a DPI concentration of approximately  $1 \times 10^{-3}$  M. Possible mechanisms for the action of the salt were examined. © 2004 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 42: 4916–4920, 2004

**Keywords:** acrylamide; dyes/pigments; onium salts; photopolymerization; radical polymerization

## INTRODUCTION

An increasing interest in three-component systems for photopolymerization in the visible region has arisen in the last few decades.<sup>1</sup> In most of these systems, a xanthenic dye and an amine, used as an coinitiator, are usually employed, with an onium salt as the third component.<sup>2,3</sup> The addition of these salts to a photoinitiator system significantly increases the polymerization rate in

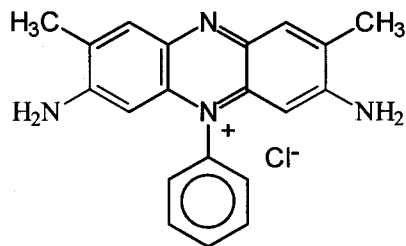
comparison with that of systems in which just a dye and an amine are used.<sup>3,4</sup> Several mechanisms have been proposed to explain the accelerating effect produced by onium salts. For radical polymerization in the presence of diphenyliodonium (DPI) salts, usually a secondary electron-transfer process involving the reduced form of the dye and DPI is proposed. This is an extra source of initiating radicals arising from the decomposition of the DPI radical.

In a previous investigation of the photopolymerization of acrylamide (AA) in water,<sup>5</sup> we observed an important increase in the polymerization rate when diphenyliodonium chloride (DPI) was added to the known initiator system safranin/triethanolamine (TEOHA; see Scheme 1 for the structural formulas). The photophysics and

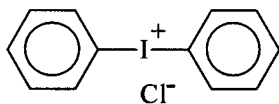
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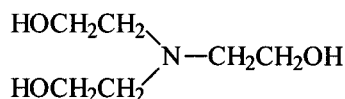
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Safranin



Diphenyliodonium chloride



Triethanolamine

Scheme 1

photochemistry of the initiator system were also investigated with static and time-resolved fluorescence spectroscopy and laser flash photolysis. The mechanism by which DPI acts is complex. Several alternatives were discussed, including an increase in the yield of active radicals, a suppression in the inhibitory effect observed at high amine concentrations, and changes in the reactivity of the excited states. The accelerating effect was found to be much more important than the increase in the yield of radicals in the initiation process.

During the fluorescence experiments, a considerable increase in the light scattering of the solutions at high concentrations of DPI was detected, although the solutions remained clear. This was attributed to the formation of aggregates of the hydrophobic DPI cations. Evidence for the aggregation of structurally related onium cations may be found in the literature. Kunz et al.<sup>6</sup> gave structural evidence for the aggregation of tetraphenylphosphonium in water. This aggregation is a phenomenon similar to the well-known aggregation of dye molecules in aqueous solutions. The predominant cause of the aggregation of these molecules has been recognized as hydrophobic interactions.<sup>7</sup> Stangret and Kamienska-Piotrowicz<sup>8</sup> in a Fourier transform infrared (FTIR) study of the interaction of tetraphenyl phosphonium cations with water molecules reported that the organic ion affected the water structure in a way

similar to hydrophobic molecules. Therefore, it can be concluded that the aggregation of DPI might take place and that it could be important in connection with the effect of the salt on the photoinitiation of vinyl polymerization.

In this work, we present a detailed study of the photophysical properties of safranin in the presence of DPI. In addition, we establish a relation between the changes in the photophysical parameters and the increase in the polymerization rate. The results reveal that important alterations in the photophysical properties of the initiator and in the polymerization rate occur for concentrations of DPI beyond  $1 \times 10^{-3}$  M, the onset concentration for the formation of aggregates. These results can be related to the effect of the medium polarity on the photophysical behavior of safranin.

## EXPERIMENTAL

### Chemicals

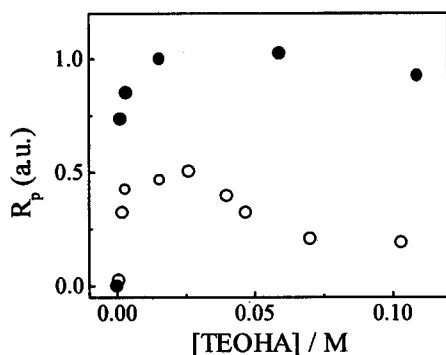
Safranin was recrystallized twice from methanol. DPI, from Aldrich, and AA (>99%, electrophoresis reagent), from Sigma, were used as received. TEOHA, provided by Aldrich, was vacuum-distilled before use. Triple-distilled water was used for the solution preparation.

## Measurements

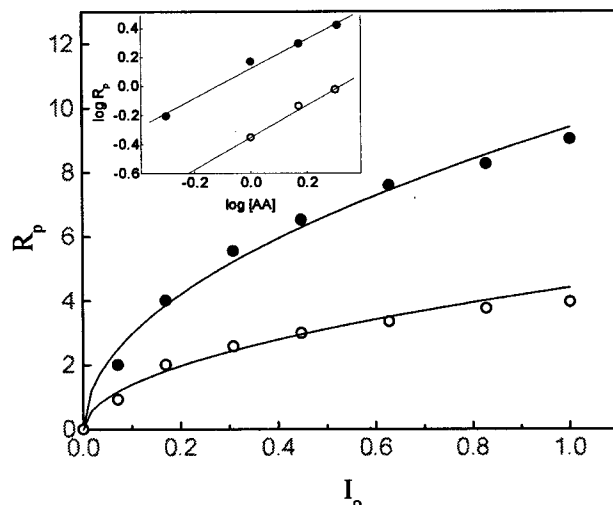
Absorption spectra were recorded with a Hewlett-Packard 8453 diode array spectrophotometer. Fluorescence and nephelometric studies were carried out with a Spex Fluoromax spectrofluorometer. The excitation wavelength was 510 nm for fluorescence determinations, and the nephelometric measurements were carried out at 500 nm with right-angle geometry. Transient absorption spectra and triplet-state properties were recorded with a Spectron SL400 Nd-YAG laser generating 532-nm pulses approximately 18 ns wide, as previously described.<sup>9</sup>

Fluorescence and triplet quantum yields were determined with a relative method with safranin T in water as a standard. In this case, the fluorescence quantum yield was 0.058, and the triplet quantum yield was 0.28 in water at 25 °C.<sup>10</sup>

Photopolymerization rates were measured dilatometrically in oxygen-free solutions. The irradiation was carried out with a monochromatic illumination system (Photon Technology International) equipped with a 150-W xenon lamp. The irradiation wavelength was set at 520 nm with a band path of 24 nm, and a cutoff filter at 500 nm was used in the light beam. To investigate the intensity dependence of the polymerization rate, the light intensity was attenuated with absorbing solutions. The safranine concentration was  $5 \times 10^{-6}$  M. All experiments were carried out at  $25 \pm 0.5$  °C. The solutions were deaerated with several freeze-thaw cycles *in vacuo* or through the bubbling of high-purity argon.



**Figure 1.** Polymerization rate ( $R_p$ ) of AA in arbitrary units as a function of the TEOHA concentration in the (○) absence and (●) presence of 0.01 M DPI.



**Figure 2.** Dependence of the polymerization rate ( $R_p$ ) on the light intensity ( $I_o$ ) in the (○) absence and (●) presence of 0.01 M DPI. The inset shows the dependence of  $R_p$  on the monomer concentration.

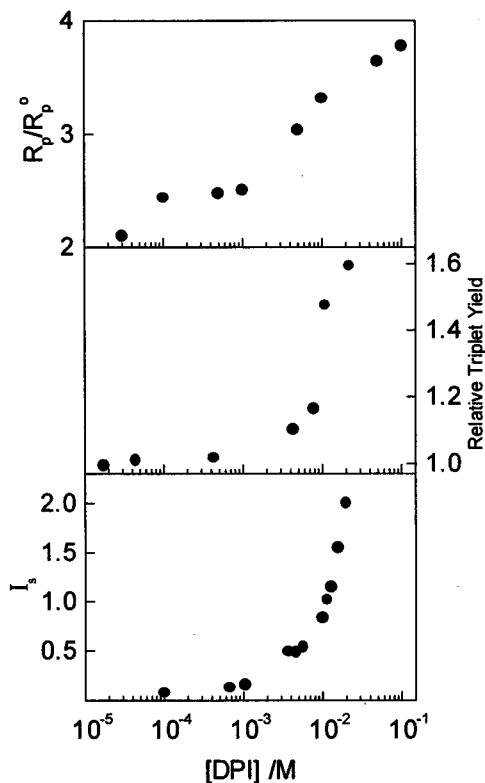
## RESULTS AND DISCUSSION

The aqueous polymerization of AA proceeded efficiently when the synthetic dye safranin was irradiated in the presence of TEOHA in the visible zone of the spectrum. The polymerization efficiency increased when DPI was added. Figure 1 shows the effect of DPI on the photopolymerization of AA photoinitiated by the safranin/TEOHA system by continuous irradiation at 520 nm. The polymerization rate increased by a factor of four, ongoing from 0 to 0.01 M in DPI at 0.1 M TEOHA.

To check the polymerization kinetics, we investigated the dependence of the polymerization rate on the monomer concentration and light intensity in the absence and presence of DPI. The results are shown in Figure 2. The solid lines correspond to an order of 1/2 on the light intensity and a unitary slope for the monomer concentration dependence. Therefore, the rate law conforms to the classic vinyl polymerization mechanism with second-order termination.

The triplet yield increased in the presence of DPI, whereas the ground-state absorption spectrum remained practically unchanged. At the same time, the fluorescence spectrum remained the same, and the fluorescence yield presented a slight increment. The quantum yield in the presence of 0.01 M DPI was 0.065.

Figure 3 shows the polymerization rate and safranin triplet yield as functions of the DPI concen-



**Figure 3.** Effect of the DPI concentration on the relative polymerization rate ( $R_p/R_p^0$ ), relative triplet yield, and light scattering of the solutions ( $I_s$ ).

tration. After a plateau in the region of  $10^{-5}$  to  $5 \times 10^{-3}$  M, a sudden increase in both quantities took place at a concentration of approximately 0.01 M. Figure 3 also shows the relative light scattering of solutions of the salt. The concentration dependence of this quantity closely resembled that of the triplet yield and the polymerization rate. The abrupt change in the light scattering may be related to the formation of aggregates of the salt. Although to our knowledge the aggregation of DPI has not been reported in detail, it has been well characterized for a number of bulky organic cations and other onium salts. This aggregation is ascribed to a hydrophobic effect reflected in an FTIR study of the interaction between water molecules and tetraphenylphosphonium cations.<sup>8</sup> The nephelometric results shown in Figure 3 correspond to solutions of the salt in the absence of the other components of the polymerization system. In the presence of 1 M AA and 0.01 M TEOHA, the scattering was less intense, but the dependence on the DPI concentration was quite similar.

Although the polymerization rate increased by a factor of about 4 at 0.01 M DPI, the triplet yield

was only 1.6 times higher. Consequently, the effect of DPI on the polymerization rate could not be ascribed only to an enhancement of the intersystem crossing. In addition, from a comparison of the relative polymerization rate and the scattering of DPI solutions (Fig. 3), two regions could be distinguished for the effect of DPI. In the first one, from  $1 \times 10^{-5}$  to  $1 \times 10^{-3}$  M, a moderate increase, by a factor of 2, could be observed. In this region, the formation of aggregates was not sensed by the nephelometric (light scattering) measurements. For concentrations higher than  $10^{-3}$  M, an important acceleration effect was noticeable, and this coincided with the increase in the nephelometric intensity. It can be concluded that this important effect of DPI on the polymerization rate could be correlated with the onset of the aggregation phenomenon of the salt.

The nature of the aggregates could not be clearly established with the experimental techniques available to us; however, the light scattering due to the aggregation of DPI was much higher than that observed for a common surfactant such as SDS in the same concentration range, within which normal micelles are formed.

Several explanations may be offered for the effect of the aggregation on the photopolymerization. First, the adsorption of the dye to the DPI aggregates may be considered, although this may be of minor importance because of the positive charge of both the dye and the aggregates. Moreover, the absorption and fluorescence of the dye remained practically unchanged, except for a minor increase ( $\approx 10\%$ ) in the fluorescence yield. On the other hand, the triplet yield increased by a factor of 1.6. This might be due to a singlet quenching by DPI by a heavy atom effect caused by the presence of the iodine atom. However, the fluorescence lifetime remained practically the same in the presence of the salt. Furthermore, the polymerization rate increased by a factor much higher than that of the triplet yield; therefore, this effect may not be the only reason for the increase in the rate.

A more plausible explanation for the increase in the polymerization rate may be the interaction of the growing chains with the aggregates. This could reduce the termination rate and also affect the propagation rate by a local concentration effect if it is assumed that the monomer presents some preference for the particles. This particulate effect may be compared with the enhanced photoinitiation activity of macrophotoinitiators.<sup>11</sup> Macromolecular photoinitiators based on thioxanthone or benzophenone in the presence of di-

ethylamino ethanol were found to more efficient than corresponding low-molecular-weight analogous. The explanations given for that case could also apply to this case, and they are in line with those mentioned previously.

## CONCLUSIONS

The addition of DPI to the safranine/TEOHA photoinitiator system produced a notable increase in the polymerization rate of AA in aqueous solutions. This acceleration effect increased appreciably at concentrations of DPI at which the light scattering by the solutions became important. It was concluded that the effect of DPI on the polymerization correlated with the aggregation of the organic cations because of a hydrophobic effect.

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