

## Material behaviour

# Relative sensitization efficiency of fluorescent probes/sensitizers for monitoring and acceleration of cationic photopolymerization of monomers



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## ARTICLE INFO

## Article history:

Received 5 September 2015

Accepted 12 October 2015

Available online xxx

## Keywords:

Cationic photopolymerization

Fluorescent probes

Sensitizers

FPT

Testing method

## ABSTRACT

The performance of a series of 1-amino-2,6-dicyano-3,5-diphenylbenzene derivatives (i.e., *meta*-terphenyls) as fluorescent molecular probes for monitoring cationic photopolymerization of monomers by the Fluorescence Probe Technique (FPT) was studied. It was found that the *m*-terphenyls accelerate the cationic photopolymerization initiated with diphenyliodonium photoinitiators at the wavelength where the photoinitiator alone does not work. Consequently, application of the *m*-terphenyls in a dual role: (a) as fluorescent probes for monitoring the cationic polymerization progress, and (b) as long-wavelength sensitizers for diphenyliodonium photoinitiators is proposed. Next, a precise method for determination of relative sensitization efficiency of the sensitizers has been devised and applied for evaluation of the performance of the *m*-terphenyl sensitizers in comparison to that of a commercial sensitizer: 2,4-diethyl-9*H*-thioxanthen-9-one.

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## 1. Introduction

Photoinitiated cationic polymerization is an important process used for a variety of applications, such as photocurable coatings, inks, adhesives, etc., that can be applied without use of solvents, so air pollution with volatile organic compounds is eliminated [1,2]. In comparison to free radical photopolymerization, cationic photopolymerization is not inhibited by oxygen, it can continue in the dark and is applicable to monomer types that are hard or impossible to polymerize by other means. Hence, it is not surprising that commercial interest in the use of cationic photopolymerization in place of the free radical route is still growing. However, the cationic photopolymerization is not without faults. The main problem is that most cationic photoinitiators absorb light in the short wavelengths range, usually below 300 nm [3]. Over the last decade, diphenyliodonium salts have been used most often as photoinitiators for cationic polymerization. The diphenyliodonium salts undergo irreversible photofragmentation in response to UV

excitation to form free radical, cationic and radical cation fragments, which undergo subsequent reactions to form neutral organic products and a strong protic acid (e.g., HSBF<sub>6</sub> or HPF<sub>6</sub>). The cationic or radical cation fragments account for initiation of cationic polymerization during irradiation with UV light, while the photo-generated strong acid is responsible for the initiation also in the dark.

The maximum absorbance of diphenyliodonium salts is in the far UV range and their absorption band tails off at about 300 nm, so that they are unable to pick up the most intense 365 nm wavelength of medium pressure mercury (MPM) lamps used as UV sources in industry, while the photoinitiator absorption at the weaker 313 nm mercury line is very low. Hence, the absorption range of currently used cationic polymerization photoinitiators does not match the emission range of the UV light sources used in industry. This makes the initiation process very inefficient and most of electrical energy supplied to the lamps is wasted.

One of the ways to increase effectiveness of the commercial photoinitiators is to use sensitizers or co-initiators that absorb light at the wavelengths where most of UV energy is emitted to form appropriate excited states, which in turn interact with the

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photoinitiator molecules, facilitating their decomposition into the initiating species. The difference between sensitizers and co-initiators is that the sensitizers remain unchanged after the polymerization process, while the co-initiators undergo transformation into other species [4]. The sensitizers used with diphenyliodonium salts include anthracene derivatives such as 2-ethyl-9,10-dimethoxyanthracene [5], 9,10-dimethylantracene [6], carbazole derivatives such as 1,3-di(carbazol-9-yl)-2-propanol [7], thiophene derivatives [8], benzothiazines [9], dithienothiophenes [10], benzodioxinones [11] and thioxanthenes [12].

On the other hand, the quality of polymers obtained by cationic photopolymerization strongly depends on the extent of monomer polymerization (“degree of cure”). When the degree of cure of a polymer coating is too low, the coating is tacky; when it is too high the coating becomes too rigid and fragile. The degree of cure depends on a multitude of factors, such as the type of monomers, type and concentration of the photoinitiator, light intensity, irradiation time, temperature, moisture of the surrounding air, etc. Hence, precise control of the degree of cure is critical for photocurable coatings quality, while not many methods can be applied for that purpose. From among the methods used so far, Fluorescence Probe Technique (FPT) has been gaining increasing significance [13,14]. The FPT method relies on measurement of changes in fluorescence characteristics of appropriate fluorescent molecular probes with changes occurring in the probe environment [15,16]. The probes are added at small concentration into photocurable compositions to sense the changes occurring during the polymerization process. However, the addition of any extra components to an existing formulation may be undesirable in some applications. In such cases, an ideal situation would be if a fluorescent probe could serve as both a cationic polymerization photoinitiator and a probe, or as a sensitizer (or co-initiator) and the probe simultaneously. Then, the photoinitiator or sensitizer used traditionally could be replaced with the dual-function component without necessity of addition of any extra components. Unfortunately, the diphenyliodonium photoinitiators do not fluoresce. Previously, we found that some aminophthalimides showed not only good probe response in cationic photopolymerization processes, but also exerted some accelerating effect on the polymerization kinetics [17,18]. Following that tendency, recently we have found that some fluorescing *o*-aminonitriles can accelerate cationic photopolymerization much more effectively than the aminophthalimides. Hence, in this paper we report the performance of a series of *o*-aminonitriles based on *m*-terphenyl skeleton in the dual role: as fluorescent probes for monitoring cationic polymerization of monomers, and as sensitizers for the diphenyliodonium photoinitiators.

## 2. Experimental

### 2.1. Materials

Triethylene glycol divinyl ether (TEGDVE, Sigma Aldrich) and diphenyliodonium hexafluorophosphate (Alfa Aesar) were applied as a model monomer and a cationic photoinitiator, respectively, while 2,4-diethyl-9*H*-thioxanthen-9-one (Sigma Aldrich) was applied as a commercial sensitizer for comparison.

The *m*-terphenyl derivatives shown in Fig. 1 were selected as the probes/sensitizers for simultaneous monitoring and acceleration of cationic photopolymerization of TEGDVE. These compounds were synthesized.

The probes **5a** and **5c–g** were synthesized by the general procedure developed by Milart and Sepioł [19,20], depicted in Fig. 2, while **5b** was obtained according to ref. [21].

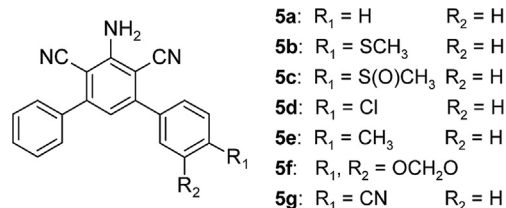


Fig. 1. The fluorescent probes studied.

### 2.2. Absorption and fluorescence characteristics

UV absorption spectra were recorded using EPP2000 C spectrometer from StellarNet, Inc. (USA) and a broadband UV/Vis deuterium-halogen light source. Fluorescence was measured with the same spectrometer. The spectra were recorded in methanol at room temperature (22 °C) using 10 mm quartz cell.

### 2.3. Preparation of thin-layer samples

The compositions used for comparison of the probes performance contained TEGDVE monomer, 1% (by weight) of the photoinitiator (Ph<sub>2</sub>I<sup>+</sup>PF<sub>6</sub><sup>-</sup>, 23.8 · 10<sup>-3</sup> mol dm<sup>-3</sup>) and the probe (4.0 · 10<sup>-3</sup> mol dm<sup>-3</sup>).

The compositions used for evaluation of the effect of the probes on the photopolymerization kinetics contained identical initial concentrations of the photoinitiator (23.8 · 10<sup>-3</sup> mol dm<sup>-3</sup>) and varied quantities of the probe **5a** (1.4 · 10<sup>-4</sup> – 2.0 · 10<sup>-2</sup> mol dm<sup>-3</sup>).

For comparison, kinetic measurements on the samples containing the same type and concentration of the photoinitiator and varied quantities of 2,4-diethyl-9*H*-thioxanthen-9-one (3.0 · 10<sup>-4</sup> – 2.0 · 10<sup>-2</sup> mol dm<sup>-3</sup>) were performed. However, as the thioxanthenone sensitizer did not fluoresce, a small quantity (5.0 · 10<sup>-4</sup> mol dm<sup>-3</sup>) of the probe **5a** was also added to each sample to enable photopolymerization monitoring.

The thin-layer samples were prepared by the procedure described previously [17]. The composition thickness between the glass slides was typically 0.08 mm, which was equivalent to an optical path length 0.092 mm, with 60° incident angle of the light beam relative to the sample surface.

### 2.4. Monitoring the cationic photopolymerization by FPT

The cure monitoring system was composed of the EPP2000C spectrometer, a sensor head, where the thin-layer sample was placed, and a UVLED emitting at 365 nm (Amecam, Poland), equipped with an appropriate power supply. The sensor head was the same as that described previously [17], except that the auxiliary UVLED was not used for this study. All measurements were done at 22 °C.

## 3. Results and discussion

### 3.1. Spectral characteristics of the probes/sensitizers

Fig. 3 shows absorption spectrum of the photoinitiator (Ph<sub>2</sub>I<sup>+</sup>PF<sub>6</sub><sup>-</sup>), and absorption and fluorescence characteristics of an example probe (**5g**). Spectral parameters of the other probes are collected in Table 1.

Fig. 3 indicates that the maximal absorbance of the diphenyliodonium photoinitiator is at about 230 nm and decreases rapidly to near zero at 300 nm. This is why photopolymerization did not occur when the composition containing that photoinitiator was illuminated with only 365 nm (±10 nm) UV light from a UVLED. The

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