Barton Esters as New Radical Photoinitiators for Flat Panel Display Applications

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A new series of photoinitiators for free radical photopolymerization based on Barton ester derivatives is developed for flat panel display applications. The absorption spectra exhibit a broad band between 320 and 420 nm. The photolysis quantum yields are very high, a fact that underlines the capability of the photoinitiators to bleach during the irradiation and thereby to lead to a moderate yellowing. Compared to commercial photoinitiators, the Barton esters display a very good efficiency. As revealed by laser flash photolysis, the dissociation rate constants are very high. Quantum mechanical computations show that the photodissociation can occur from both the excited singlet and triplet states.

Keywords: photoinitiator, laser spectroscopy, photopolymerization

1. Introduction

Free radical photopolymerization is now a mature technology that is applied in many different fields ranging from coatings and paints to microelectronics or optics. Many different photoinitiating systems are now commercially available that offer wide possibilities to cover these different applications. However, there is still a need to develop new photoinitiators exhibiting improved properties or suitable for new applications.

More than forty photoinitiators are now commercially available, most of them being based on the benzoyl chromophoric group [1-3]. Further development in that field requires a deep understanding of the basic chemical processes involved in the photoinitiator step. Many efforts were devoted during the last decade to understand the molecular details that control the photocleavage reaction in such systems. Recent studies based on time-resolved laser absorption spectroscopies in the nanosecond and picosecond time-scale or time-resolved photothermal techniques in combination with molecular modeling calculations performed at high level of theory were used to investigate the mechanisms involved. This approach was shown to afford a fine prediction of the reactivity of the photoinitiating systems [4-12].

In the field of flat panel displays, an important issue is the production of color filters or color mosaic systems. Red, green, blue or black dyes or pigments are added to the light-sensitive resin formulation. Therefore, the photoinitiating system has to meet particular requirements. Among them, the absorption property in the presence of the
pigment and the photobleaching capability are important features.\[13\]
Barton esters were introduced in the 1980s as radical generators leading to chemical amplification. These compounds are known to have intense absorption bands centered around 350-360 nm. Additionally, they undergo a fast photobleaching under light excitation. Among the different derivatives already synthesized, N-hydroxy-pyridine-2(1H)-thiones are the most usual representatives of this family of radical generators.\[14-15\]
In this paper a new series of radical photoinitiators, based on Barton ester derivatives, is proposed. The high quantum yield of photocleavage, the photobleaching ability of the molecules under irradiation make these compounds as good candidates for flat panel display applications.

2. Experimental

2.1. Materials

Barton esters (Scheme 1) were synthesized according to procedures known in the literature.\[16-18\] The other compounds used are commercially available.

![Scheme 1: Barton esters studied.](image)

2.2. Photolysis

The photolysis experiments were performed on 120 cm³ of acetonitrile solution of 6.3x10⁻³ mol/dm³ of 1. The irradiation system consists in a high pressure iron iodide lamp (UV unit type EL200411a SACK) operating at about 1500W/cm² at a distance of 90 cm.

2.3. Photopolymerization

Photopolymerization kinetics were carried out on model formulation based on SR 349 (Sartomer) and 1% of photoinitiator. All the samples were sandwiched between two polypropylene films in order to avoid oxygen diffusion. In that case, the irradiation was performed under the polychromatic light delivered by a Hg/Xe Lamp (LC6, Hamamatsu) at 50% of its maximal intensity for 20 s. The disappearance of the IR absorption of the acrylic double bond is followed at 1635 cm⁻¹ with a rapid-scan FTIR spectrometer (Vertex, Bruker). The maximum rates of polymerization Rp were deduced from the linear part of the conversion curves.\[12\]
All the compounds were tested in a typical resist made from methyl ethyl ketone (31.32 parts), 1-methoxy-2-propanol (Dowanol PM, 31.32 parts), polyacrylate-co-methacrylate (MW=34000, 7.30 parts) as a binder, a mixture of methacrylate / butylacrylate / methacrylic acid (BF3713 at 20%, 18.20 parts), trimethylolpropane triacrylate (10.94 parts) and the photoinitiator (0.50 part). The formulations were spread on an anodised aluminium support by a bar coating #2. The thickness of the dry film was about 3 μm. The solvent was removed by heating at 80°C for 2 minutes.

A standardized negative test film UGRA Control Wedge 1982 with 13 steps of different optical density (in the range between 0.15 and 1.95) was placed on the surface of the dry film. The light exposure was carried out using an high pressure iron iodide lamp (UV unit type EL200411a SACK), at a distance of 90 cm. The exposure time was calibrated to reach a total intensity about 500 mJ/cm².

After exposure, the film was developed by dipping with an aqueous solution of sodium lauryl sulphate, 2-phenoxyethanol, nonanoic acid diethanolamine salt, for 20 s at 25 °C.

2.4. Molecular modeling

All quantum calculations were carried out using the hybrid functional B3LYP and the
6-31G* basis set. Although this medium basis set would not lead to accurate results, it represents a good compromise between accuracy and computation time. Potential energy surfaces (PES) were calculated by optimizing the ground state geometry with a constrained molecular coordinate and performing an excited state calculation on the resulting structure at the TDDFT level.[19]

3. Results and Discussion

3.1. Absorption properties and photolysis

The absorption properties of 1 to 5 in acetonitrile are collected in Table 1. All the compounds exhibit an intense absorption band at ca. 363 nm with important extinction coefficients, in line with data already reported. [20]

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>( \log (\varepsilon \text{ (M}^{-1}\text{cm}^{-1})) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>363</td>
<td>3.8</td>
</tr>
<tr>
<td>2</td>
<td>363</td>
<td>3.8</td>
</tr>
<tr>
<td>3</td>
<td>364</td>
<td>3.7</td>
</tr>
<tr>
<td>4</td>
<td>363</td>
<td>3.8</td>
</tr>
<tr>
<td>5</td>
<td>364</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Table 1: Absorption properties of the compounds in acetonitrile.

The photolysis experiments were performed on 1 (6.3x10^{-5} M) in acetonitrile. The spectra shown in Figure 1 were collected at variable time from 5 to 90 s.

![Plot of photolysis of 6.3x10^{-5} M acetonitrile solution of 1.](image)

Figure 1. Photolysis of a 6.3x10^{-5} M acetonitrile solution of 1.

A total bleaching of the absorption band at 363 nm is observed. On the contrary, the growth of an absorption band is detected at 238 nm. The isobestic point at 223 nm is typical for a conversion of the photoinitiator into absorbing photoproducts within one chemical step. The disappearance of the absorption band is merely attributed to a cleavage reaction as described in Scheme 2. The photolysis of Barton esters has been already reported to be very efficient with quantum yield of 3-4 in solution, confirming the involvement of a chain reaction. [20] The photoproducts are expected to contain the pyridylthiyl moiety. A hypsochromic effect such as observed in Figure 1 at 288 nm was already discussed for the photolysis of 2-pyridinethione in isopropanol. [21]

\[
\text{hv} \quad \text{S} \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{R} \rightarrow \text{O} \quad \text{O} \quad \text{R} \quad + \quad \text{S}^* \quad \text{N} \quad \text{O} \quad \text{CO}_2 \quad + \quad \text{R}^*
\]

Scheme 2: Mechanism proposed for the photodissociation of Barton esters.

3.2 Photocleavage reaction

The photocleavage reaction that produces thyl radicals was already shown to proceed within the picosecond time scale. [20] Molecular modeling was performed in order to obtain information about the photocleavage reaction. Potential energy surfaces for the N-O bond dissociation were computed at a TD-B3LYP/6-311++G** level on the B3LYP/6-31G* optimized ground state geometry for a model compound bearing a methyl group as a O-substituent. The energy of the ground state \( S_0 \), the first excited state \( S_1 \) and the lowest triplet state \( T_1 \) are reported in Figure 2 as a function of the N-O bond length. The computed N-O bond dissociation energy is 28.2 kcal/mol. Both the first excited singlet state and the triplet state are dissociative with only small activation energies about 5 and 7 kcal/mol for \( S_1 \) and \( T_1 \), respectively. These activation energies are rather small and therefore, Barton esters can readily cleave from the singlet excited state, a fact that is in line with the fast cleavage process observed in picosecond absorption spectroscopy [20]. A cleavage from the lowest triplet state is
also expected: this reaction can occur through the sensitization with a triplet energy donor. Due to the difficulty to locate a local minimum, it was not possible to compute the relaxed triplet state. Therefore, the triplet energy of the model compound was computed as the spectroscopic one using a time-dependent procedure on an optimized ground state. The resulting value of 53 kcal/mol is low enough to anticipate a good sensitization process from usual triplet sensitizers like isopropylthioxanthone.

![Energy vs N-O distance](image)

Figure 2. Potential energy surfaces of the ground state (diamond), the first excited singlet state (square) and the lowest triplet state (triangle) for a methyl substituted Barton ester.

From these results, the photocleavage from both the first excited singlet state and the lowest triplet state can occur. Direct excitation will favor a singlet state photodissociation and photosensitization would favor a triplet state one. All these calculated data are in agreement with the high photochemical reactivity of these compounds that is experimentally observed.

3.3 Photopolymerization experiments.

In order to compare the relative efficiency of the compounds as radical photoinitiators, a set of experiments was performed in SR 349 as a photopolymerizable formulation. The photopolymerization profiles are shown in Figure 3 and the corresponding results are gathered in Table 2. From this table, it can be seen that the compounds bearing an alkyl substituent give rise to a fast photopolymerization with no inhibition time. On the contrary, compound 5 containing a phenyl group has a poor efficiency. The maximum conversion obtained reach ca. 35% after 20 s of irradiation.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$100xR_p/[M]_0$</th>
<th>maximum conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>52</td>
<td>31</td>
</tr>
<tr>
<td>2</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>31</td>
</tr>
<tr>
<td>5</td>
<td>2.2</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 2: Rates of polymerization and final conversion of SR349 in the presence of 1% photoinitiator under the Hg/Xe lamp exposure.

This result might be explained by the fact that the photopolymerization process occurs at a temperature lower than the Tg of the material, leading to a fast gelification of the medium.

![Conversion vs Time](image)

Figure 3. Conversion curves of SR 349 as photopolymerizable composition with 1% of photoinitiator.

It is of prime interest to note that the previous results were obtained in a fluid polymerizable medium. In photoresist applications, the use of binders makes the medium much more rigid and therefore the diffusion processes are completely affected.

<table>
<thead>
<tr>
<th>Compound</th>
<th>number of step without PVA</th>
<th>Number of step with PVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3-4</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>3-4</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>//</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 3: Results of the UGRA negative test film after development.

Experiments using photoresists were carried out. The sensitivity of the different
compositions was characterized by the number of steps that can be read from the UGRA negative test film after development: the higher the number, the more sensitive is the tested composition. Every operation was carried out under yellow light. Some experiments were performed using a topcoat of 7.5 % PVA aqueous solution used to avoid oxygen inhibition. The results are listed in Table 2. It can be seen that 1 and 2 lead to very sensitive compositions usable in photoresists. Keeping in mind that these molecules exhibit interesting absorption properties as well as excellent capability to bleach under irradiation, these photosensitivity experiments show that Barton esters are good photoinitiators for flat panel display applications.

4. Conclusion

In this paper, the ability of Barton ester derivatives to initiate a free radical photopolymerization was investigated. Photolysis experiments show that a total photobleaching of the photoinitiator occurs under irradiation at wavelengths higher than 320 nm. A mechanism is proposed to account for this behavior. It was shown from molecular modeling computations that the cleavage reaction can occur from both the excited singlet state and the lowest triplet state. The measurement of the rates of polymerization in fluid medium allows to underline the highest efficiency of the alkyl substituted compounds. In photoresist film, a good sensitivity was also found for these compounds.

Acknowledgement: Thanks are due to C. Peiffer for technical assistance.

References