High Performance Photoinitiating Systems: Application to Holographic Grating Recording

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Photopolymerization reaction can be used in self-developing photopolymerizable resin to recording holographic gratings. In this work, the efficiencies of two and three component photoinitiating system for holographic recording are analyzed in term of photopolymerization and grating diffraction yield kinetics. The selected systems are based on a visible dye, electron donor and electron acceptor. Time resolved and steady state spectroscopic studies of the photoinitiators are presented. This detailed photochemical study outlines the possible existence of photocyclic initiating systems where the dye is regenerated during the photochemical process. To study the impact of photoinitaiting system on the hologram grating formation, diffraction curves are compared to those of monomer to polymer conversion. This work outlines the importance of the photochemistry on final holographic material properties.

Keywords: Photochemistry, Holography, Photopolymer, Photocyclic initiating system

1. Introduction

Photopolymerization reaction can be used in self-developing photopolymerizable resin to record holographic diffraction gratings. The irradiation of holographic resin formulation by a sinusoidal light intensity pattern induces inhomogeneous photopolymerization in the medium which leads to microstructuration of the polymer. A sinusoidal modulation of the refractive index is thus obtained in the photopolymerizable matrix.[1,2] It was demonstrated that the efficiency of light conversion into chemical energy directly impacts the refractive index modulation [3] and the final properties of the holographic grating. The aim of this paper is to study the effect of three-component photoinitiating system (PIS based on a dye, a coinitiator and a redox additive) on the efficiency of holographic grating recording. For this purpose, two different three-component photoinitiating systems were chosen to react through two different photochemical pathways, as demonstrated by laser flash photolysis studies. Free radical photopolymerization experiments and holographic recordings using these PIS were performed and compared.

2. Experimental

2.1. Materials

Safranine O (SFH⁺) and Ethyl 4-(dimethylamino)benzoate (EDB) were purchased from Sigma-Aldrich. 4-methyl-phenyl-[4-(2-methylpropyl)phenyl]iodonium hexafluorophosphate (I250) was gift from Ciba Spa. (Switzerland). 2-(4-Methoxy-phenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine (TA) was a gift from Produits Chimiques Auxiliaires et de Synthèses (Longjumeau, France).
2.2. Holographic material

The holographic resin was a mixture of different monomers and additives [4]. This self-developing formulation contained:
- 45 wt% of a hexafunctional aliphatic urethane acrylate oligomer (Ebecryl 1290, Cytec);
- 22.5 wt% of 1,1,1,3,3,3-hexafluoroisopropyl acrylate and 22.5 wt% of vinyl neoonanoate, 5 wt% of N-vinyl-2-pyrrolidinone, 5 wt% of trimethylpropane tris(3-mercaptopropionate) (Sigma-Aldrich; France). The chemical structures of the reagents used for the preparation of holographic resin can be found in ref [5].

2.3. Measurements

2.3.1. Cyclic voltammetry

Redox potentials were measured by cyclic voltammetry (Princeton Applied Research 263A potentiostat, 1 V/s scan rate) using platinum electrodes and a saturated calomel reference electrode (KCl in methanol). Measurements were performed in acetonitrile using 0.1M of tetrabutylammonium hexafluorophosphate (Aldrich) as supporting electrolyte. The samples were bubbled with argon. Ferrocene was used as standard [6].

2.3.2. RT-FTIR measurements

The study of photopolymerization kinetics was carried out by real-time FTIR (RT-FTIR) technique (Vertex 70 FTIR Bruker Optik), equipped with a MCT detector working in the rapid scan mode. The IR spectra were then recorded during sample irradiation using a green laser diode emitting at 532 nm (Roithner Lasertechnik, 50 mW). The irradiation intensity was adjusted to 22.5 mW/cm² on the sample. Experiments were carried out by laminating the resin between two polypropylene films and two CaF₂ windows (25 µm thickness). The kinetics of the polymerization were measured by following the disappearance of the C=C bond stretching signal at 1637 cm⁻¹.

2.3.3. Spectroscopy measurements

Laser flash photolysis experiments (LFP) were carried out on an Edinburgh Instruments LP900 transient absorption analysis system using an excitation wavelength at 532 nm with a nanosecond Nd-YAG laser (Powerlite 9010, Continuum).

2.3.4. Holographic recording

The samples were prepared by sandwiching the photopolymerizable formulation between two glass-substrates (20 µm thickness). A sinusoidal light pattern is generated by the interferences of two 514 nm (Coherent Innova 308C Argon Ion laser, see Scheme 2) incident laser plane waves on the sample (22.5 mW/cm²). The fringe spacing is adjusted to ca. 0.9 µm.

The fact that no chemical post-treatment was needed for this recording medium, allows the simultaneous follow up of the process during exposure with an inactinic reading light beam (HeNe laser at 633 nm, Scheme 2). The diffraction efficiency at 633 nm (η) was defined by the ratio of the intensity of the first diffraction order to the diffracted plus transmitted light intensities in order to rule out Fresnel losses in the determination of the grating diffraction efficiency.

3. Results and discussion

3.1. Molecular photochemistry

In this work two different three-components photoinitiating systems were analyzed, both being based on the same dye Safranine O (SFH⁺) and the same electron donor (the amine EDB). The third redox additive was either a triazine (TA) or an
iodonium salt (I250) as electron acceptor.

A thermodynamical analysis of the photoinduced electron transfer (PET) between the excited dye and the coinitiator can be done by calculating the corresponding Gibbs free energy change \( \Delta G_{et} \):

\[
\Delta G_{et} = (E_{ox} - E_{red}) - E^* + C
\]

where \( E_{ox} \) and \( E_{red} \) are the half-wave oxidation and reduction potentials for the donor and the acceptor (in V), respectively, and \( E^* \) is the energy of excited state (in eV, see ref. [7,8]). The coulombic term \( C \) is usually neglected in polar solvent. The calculated Gibbs free energy values \( \Delta G_{et} \) for the different dye-coinitiator combinations are gathered in Table 1 (the oxidation potential of EDB is 1.07 V and the reduction potential of TA and I250 are -1.12 V and -0.82 V, respectively). The calculated \( \Delta G_{et} \) values indicate that the PET process is thermodynamically favorable between both the singlet and the triplet excited states of SFH+ and the electron donor coinitiator EDB. The photoinduced electron transfer is also thermodynamically favorable for the iodonium salt acceptor I250. For triazine A the picture is quite different: the PET is exergonic for the singlet excited state \( 1SFH^+ \) of the dye, but endergonic for the excited triplet state \( 3SFH^+ \).

Table 1. \( \Delta G_{et} \) and quenching rate constant \( k_q \) for PET between Safranine O excited singlet (\( 1SFH^+ \)) and triplet (\( 3SFH^+ \)) states and the coinitiators.

<table>
<thead>
<tr>
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<th>Singlet state</th>
<th>Triplet state</th>
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<tbody>
<tr>
<td>( \Delta G_{et} ) (eV) / ( k_q ) (M(^{-1}).s(^{-1}))</td>
<td>'SFH'</td>
<td>'SFH'</td>
</tr>
<tr>
<td>EDB</td>
<td>-0.72/1.9 ( \times 10^{10} )</td>
<td>-0.14/2.4 ( \times 10^{8} )</td>
</tr>
<tr>
<td>I250</td>
<td>-0.73/7.2 ( \times 10^{10} )</td>
<td>-0.15/8.0 ( \times 10^{7} )</td>
</tr>
<tr>
<td>TA</td>
<td>-0.43/3.3 ( \times 10^{9} )</td>
<td>0.15/7.3 ( \times 10^{8} )</td>
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</table>

The quenching rate constants were measured by LFP for triplet states and fluorimetry for singlet states (see Table 1) and are found to be in good agreement with \( \Delta G_{et} \) values. The quenching rate constant of \( 3SFH^+ / EDB \) is higher than for TA or I250 by three orders of magnitude. Therefore, it is awaited that \( 3SFH^+ \) reacts first with EDB in the holographic resin. The viscosity of the resin being higher than that of acetonitrile (see ref. [5]), the maximum rate constant of PET should be lower than \( 10^8 \) M\(^{-1}\).s\(^{-1}\) in the resin. This will not affect the predominance of reactivity for EDB compared to TA and I250. However, this effect will limit the reactivity of the short-lived singlet excited compared to long-lived triplet excited state. As a consequence the singlet excited state pathway can be neglected. Figure 1 shows that the quenching of SFH+ by EDB leads to the formation of the semi reduced form of SFH+ (SFH*) which could be observed at 430 nm. Consequently, one can observe a bleaching of the ground state at 510 nm (Fig. 1).

The addition of small amounts of I250 to a SFH+ / EDB system leads to a decrease of the transient signal at 430 nm, evidencing a reaction between SFH* and I250 (Fig. 1). Interestingly, the ground state photobleaching is less pronounced, showing that the dye is partly recovered during this reaction.

Fig. 1. Laser Flash Photolysis study of SFH+/EDB/I250 PIS. (Up) Semi reduced form SFH* observed at 430 nm, (Down) Ground state photobleaching recovery observed at 510 nm.

Fig. 2. Proposed mechanisms of (up) parallel three component photoinitiating system (PIS) SHF+/EDB/TA, and (down) photocyclic initiating system (PCIS) SHF+/EDB/I250.
As a matter of fact, the addition of I250 turns the behavior of the system into a photocyclic initiating system (PCIS). Figure 2 (bottom) shows the corresponding proposed mechanism.

Surprisingly, replacing I250 by triazine A (TA) does not lead to the same behavior. It has been observed (see ref. [4]) that no dye regeneration occurs and two competitive parallel reactions are obtained as display on Fig. 2 (up).

3.2. Photopolymerization efficiency

The ability of the different dye/coinitiators combinations to start free radical polymerization was explored by time-resolved FTIR (RT-FTIR). The evolution of monomer conversion with time is displayed on Fig. 3. It can be seen that two components SFH+/electron acceptor PIS (i.e. TA and I250) lead to slow rates of conversion \( R_c \) (see Table 2), in good agreement with the low values of the quenching rate constants \( k_q \) (vide supra). Then, SFH+/EDB photoinitiating system presents a higher reactivity, i.e. a higher rate of polymerization \( R_C \), as can be seen in Table 2. This behavior is in very good agreement with the high \( k_q \) value measured for SFH+/EDB.

On the other hand in the system SFH+/EDB/TA, no photocycle is taking place, the whole mechanism is merely the addition of two competitive PET. This leads to a slightly higher quenching of the triplet excited state due to higher concentration of quenchers ([EDB] + [TA]). Obviously, this PIS leads to lower radical concentration compared to SFH+/EDB/I250. As no recovery of the dye occurs during the process, the whole radical concentration is equal to the initial dye concentration (see ref [9] for details), i.e. 10^{-6} to 10^{-5} M. Thus this competitive PIS presents lower reactivity compared the photocyclic PIS.

<table>
<thead>
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<th></th>
<th>( R_c(s^{-1}) )</th>
<th>( C_{max}(% ) )</th>
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<tbody>
<tr>
<td>SFH+/EDB</td>
<td>1.3</td>
<td>37.4</td>
</tr>
<tr>
<td>SFH+/TA</td>
<td>0.42</td>
<td>37.3</td>
</tr>
<tr>
<td>SFH+/I250</td>
<td>0.5</td>
<td>45</td>
</tr>
<tr>
<td>SFH+/EDB-TA</td>
<td>2.1</td>
<td>50.7</td>
</tr>
<tr>
<td>SFH+/EDB-I250</td>
<td>5.0</td>
<td>68</td>
</tr>
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3.3. Holographic grating recording

Photopolymerization process occurring during holographic grating recording is different from homogeneous photopolymerization as done previously: indeed, a three-dimensional image is built through the sinusoidal irradiation of the interference pattern [10-12]. This induces inhomogeneous photopolymerization of the photosensitive recording medium at the sub-micrometer scale, leading to refractive index modulations in the polymerized matrix (see Scheme 2).
Many physical and chemical processes are involved in the holographic recording: photochemical conversion of the sensitizer, polymerization of the monomer, mass transport, vitrification of the polymer matrix. The efficiency of the different PIS towards holographic grating recording was studied by measuring the diffraction yield of the grating during irradiation time. Diffraction yields curves are displayed on Fig. 4. The two systems SFH⁻/TA and SFH⁻/I250 behave slightly differently, the later being a little bit faster, (see $R_\eta$ in Table 3). Interestingly, the system SFH⁻/EDB exhibit a very good reactivity, quite close to SFH⁻/EDB/TA. These two systems lead to high final diffraction yields.

Table 3. Holographic grating recording results. $R_\eta$ represents the maximum rate of grating formation, $\eta_{\text{max}}$ is the final diffraction yield.

<table>
<thead>
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<th>$R_\eta$(s⁻¹)</th>
<th>$\eta_{\text{max}}$</th>
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<tbody>
<tr>
<td>SFH⁻-EDB</td>
<td>0.26</td>
<td>0.89</td>
</tr>
<tr>
<td>SFH⁻-TA</td>
<td>0.08</td>
<td>0.88</td>
</tr>
<tr>
<td>SFH⁻-I250</td>
<td>0.065</td>
<td>0.91</td>
</tr>
<tr>
<td>SFH⁻-EDB-TA</td>
<td>0.31</td>
<td>0.91</td>
</tr>
<tr>
<td>SFH⁻-EDB-I250</td>
<td>0.70</td>
<td>0.62</td>
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</table>

The photocyclic initiating systems SFH⁻/EDB/I250 gives, by far, the highest rate of grating formation. In only few seconds, a diffraction yield of unity is reached. However, this value rapidly falls down to a final value of 0.62. This could be explained in term of over modulation of the refractive index, too fast hardening of the medium, photopolymerization in the dark fringes, etc…

Fig. 5. Linear relationship between rate of conversion $R_C$ and rate of grating formation $R_\eta$.

Nevertheless, the fact that a value of unity could be reached within 4 seconds opens new opportunity for fast holographic recording. Deeper investigation of the coupling between the resin and the PCIS is needed.

Finally, a linear correlation between $R_C$ and $R_\eta$ is observed in Table 3 and Fig. 5. This indicates that the rate of radical production directly affects the rate of hologram formation, i.e. the refractive index modulation due to inhomogeneous polymerization of the holographic resin.

**Conclusion**

In this work, the effect of the photochemistry of photoinitiating system on the efficiency of holographic diffraction grating recording was studied. A very sensitive system was obtained by combining a PCIS and a holographic resin, reaching an unity yield of diffraction in less than 4 seconds. A linear relation was found between the maximum rate of hologram formation $R_\eta$ and the maximum rate of polymerization $R_C$.

**References**