Dual-cure Photo-thermal Initiating System for Cationic Polymerization of Epoxy under LED Visible Light

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The development of new initiating systems for epoxy resin curing remains a highly interesting topic, especially for composites and coatings applications. Among all the possibilities existing to cure an epoxy resin, recent works have highlighted novel photo-thermal cationic initiators based on pyrylium salts. Interestingly, absorption spectra of trisubstituted pyrylium salts extend up to the visible region, a feature that was not exploited yet. In this paper, the pyrylium salts absorption spectra were predicted using Density Functional Theory. It is shown that accurate prediction of UV-Vis spectra can be made at relatively moderate level of theory. Then, visible photopolymerization of epoxy resin was performed under mercury lamp and 395 nm LED. Finally, a photoinduced thermal frontal polymerization of a thick sample of epoxy resin was performed by prompting the reaction at 395 nm. This work opens new opportunity in the polymerization of thick materials such as for composites.

Keywords: Dual-cure, Pyrylium, Epoxy, Cationic polymerization

1. Introduction

Dual-cure systems have attracted a considerable interest these last years. Indeed, a wide range of new processes and applications are now open with this kind of concept. For example, designing multi-wavelength or photo-thermal curing allows addressing certain issues for a given system. As example, the decrease of light penetration with increasing thickness represents a serious drawback for thick, pigmented coatings and fiber-reinforced composites. Therefore, the concept of dual-cure initiating systems based on both photo-thermal curing appears as a promising alternative to solve the issue [1-14]. Indeed, the combination of a photochemical polymerization promoting a thermal curing has rendered possible the curing of thick samples. In this process, the photochemical reaction allows the curing of the surface within few seconds whereas the thermal reaction guarantees a full curing in depth. Moreover, the thermal process can also be used to complete the curing of the epoxide resin in shadowed areas, typically in the case of 3D parts. In the best cases, the photochemical process would also speed up the thermal curing to perform a photoinduced thermal frontal polymerization [1-14].

Recently, pyrylium salts have been reported as new photo/thermal initiators for epoxy monomers under UV irradiation or under heat [1-4]. In these works, the versatility of dual-cure initiating systems based on pyrylium salts has been demonstrated. It has been shown that 2,4,6-triphenylpyrylium tetrafluoroborate (TPP⁺) behave is an efficient cationic photo- and thermal initiator, especially in the presence of small amounts of vinyl ether or hydrogen peroxide as cointiators. These multiples abilities enable to perform photoinduced thermal frontal polymerization of a cycloaliphatic diepoxy resin under UV-light.

Interestingly, TPP⁺ exhibits good absorption in visible range. This feature would allow promoting TPP⁺ as photo/thermal initiator for visible range and more particularly for LED irradiation. Indeed,
due to their characteristics, LED systems are quite attractive. They provide narrow irradiation band, long lifetime and low heat generation. Moreover, the use of 395 to 405 nm LED is generally preferred to avoid harmful radiations related to conventional mercury lamps.

In this work, a benchmark for the prediction of singlet electronic transitions energies of TPP⁺ was performed with Time-Dependent Density Functional Theory (TD-DFT) using various hybrid functionals and basis sets. Then, the TD-DFT method giving the best agreement with the experimental values was used to predict the absorption properties of several pyrylium salts, highlighting the ones which are able to absorb at 395 nm. Finally, on the basis of TPP⁺, the dual-curing of an epoxy resin was performed under mercury lamp and 395 nm LED demonstrating the possibility to promote the polymerization of thick epoxy resin by blue light.

2. Experimental

Computations were performed using Gaussian 09 suite of programs. UV-spectra of pyrylium salts were performed in acetonitrile on a SPECORD 210 spectrophotometer from AnalytikJena.

2,4,6-triphenylpyrylium tetrafluoroborate (TPP⁺), anhydrous propylene carbonate, isobutylvinylether were purchased from Aldrich and hydrogen peroxide from Carlo Erba. The cycloaliphatic diepoxy resin was (3,4-epoxycyclohexane)-methyl-3,4-epoxycyclohexylcarboxylate (Genomer 7210, Rahn). The monofunctional oxetane resin was 3-ethyl-3-hydroxymethyl-oxetane (OXT-101, Toagosei).

Photopolymerization experiments were carried out in transmission mode using RT-FTIR (Vertex 70 FTIR spectrometer, Bruker Optik) equipped with MIR and NIR light sources and MCT detector working in rapid scan mode. This allows 4 scans.s⁻¹ average collection data rate, with a 4 cm⁻¹ resolution. Polymerization profiles were recorded during 150 s of irradiation using an Hg-Xe lamp with a reflector at 365 nm (Hamamatsu, 150 W), or 395 nm LED (Roithner LaserTechnik). The incident light intensity fixed to 70 mW.cm⁻². The pyrylium salt was solubilized in propylene carbonate at 25/75 weight ratio and then added at 3 wt% in epoxide resin. The formulation was deposited on a BaF₂ pallet support using a calibrated bar coater of approximately 20 μm of thickness. The polymerization kinetics were measured by following the disappearance of the epoxy vibration band at 789 cm⁻¹. Thus, the conversion was calculated as:

\[
\text{Conversion (\%)} = \left(\frac{A_0 - A_t}{A_0}\right) \times 100
\]

where \(A_0\) and \(A_t\) stand for the absorbance at 789 cm⁻¹ at time zero and time t, respectively.

Temperature measurement following the polymerization front displacement was measured with a DaqLab 5000 (Fourier System) using K type thermocouples.

Figure 1 describes the dual-cure setup. Test tube with mixture is oriented in a vertical position and irradiated with the LED. Then IR camera records the temperatures of the sample to follow the displacement of front.

![Figure 1: Setup for frontal polymerization.](image)

3. Results and discussion

3.1. Computation of singlet transitions energies

With the target to select the best functional and basis set for the accurate computation of singlet electronic transition of pyrylium salts, a
benchmark method was used. For this purpose, different basis sets of increasing level were tested to gradually increase the accuracy of the computation. Then, the same kind of work was carried out on different functionals with the best basis set previously selected. The benchmark was done on TPP+.

TPP+ exhibits two important maxima of absorption at 355 nm (3.49 eV) and 405 (3.06 eV) nm, in acetonitrile (Fig. 2). These bands are usually denominated as \( y \) for 355 nm and \( x \) for 405 nm [15-17].

Table 1. Benchmark of basis sets on TPP+ using PBE1PBE as functional.

| Basis sets | Y band (Error) (eV) | X band (Error) (eV) |
|------------|---------------------|---------------------|
| 6-31G      | 3.41 (0.08)         | 3.11 (0.05)         |
| 6-31G*     | 3.45 (0.04)         | 3.17 (0.11)         |
| 6-31G**    | 3.46 (0.03)         | 3.17 (0.11)         |
| 6-31+G**   | 3.43 (0.06)         | 3.14 (0.08)         |
| 6-311+G**  | 3.44 (0.05)         | 3.14 (0.08)         |
| 6-311++G** | 3.44 (0.05)         | 3.14 (0.08)         |
| Experiment | 3.49                | 3.06                |

To find the most adapted basis set, PBE1PBE functional was fixed and the basis set was gradually changed from 6-31G to 6-311++G**. The results obtained were collected in Table 1. As expected, it can be seen that the basis set plays an important role in the computation. Increasing the basis set from 6-31G to 6-311++G** leads to a plateau value above the 6-31+G* level. 6-311+G** appears as a suitable basis set to continue the benchmark of functionals.

For benchmarking the functionals, Becke three and one parameters hybrid functionals were selected (B1LYP, mPW1PW91, B3LYP, O3LYP, B3PW91), as well as functional including dispersion (PBE1PBE) and long-range-corrected ones (LC-wPBE, LC-BLYP, CAM-B3LYP). The computations were performed using polarizable continuum model calculation (PCM) to take into account the effect of solvent on the singlet transition energies. The results obtained are collected in Table 2.

The results obtained in Table 2 are very different depending the functionals used. Becke one parameter functionals and functionals including dispersion show an average error of around 0.05 eV, whereas Becke three parameters functionals and long-range-corrected functionals have an average error up to 0.06 eV. B1LYP, mPW1PW91 and PBE1PBE are the three most accurate functionals tested in this paper with 6-311+G** basis set. Taking into account the values of the singlet energies (3.49 eV and 3.06 eV), it should be noted that an error of 0.05 eV corresponds to an error of around 6 nm on the absorption spectrum. The B1LYP functional shows the lowest error for the lowest job CPU time. Therefore, it was selected for the singlet states energy computation of different pyrylium salts.

Eight others pyryliums salts (Fig. 3) were analyzed by UV-Vis spectroscopy and the results compared to computation data (Table 3) using B1LYP/6-311+G** with PCM correction. The computation results exhibit an average error of only 0.12 eV (or 10 nm). Consequently, B1LYP/6-311+G** with PCM correction appears

Table 2. Benchmark of functionals on TPP+ using 6-311+G** basis set with polarizable continuum model calculation (PCM).

| Functionals   | Y band (Error) (eV) | X band (Error) (eV) | Average error (eV) | Job CPU time |
|---------------|---------------------|---------------------|--------------------|--------------|
| B1LYP         | 3.45 (0.04)         | 3.11 (0.05)         | 0.045              | 19h 17min    |
| mPW1PW91     | 3.5 (0.01)          | 3.16 (0.1)          | 0.055              | 23h 38min    |
| B3LYP         | 3.34 (0.15)         | 3.03 (0.03)         | 0.090              | 20h 40min    |
| B3PW91       | 3.38 (0.11)         | 3.07 (0.01)         | 0.060              | 21h 02min    |
| O3LYP         | 3.2 (0.29)          | 2.97 (0.09)         | 0.190              | 20h 01min    |
| PBE1PBE       | 3.5 (0.01)          | 3.16 (0.1)          | 0.055              | 23h 30min    |
| LC-wPBE       | 4.36 (0.87)         | 3.78 (0.72)         | 0.795              | 27h 53min    |
| LC-BLYP       | 4.43 (0.94)         | 3.8 (0.74)          | 0.840              | 37h 10min    |
| CAM-B3LYP     | 3.92 (0.43)         | 3.46 (0.4)          | 0.415              | 39h 15min    |
to be a quite accurate computation method to predict singlet state transition energy of trisubstituted pyrylium salts.

3.2. From Hg lamp to LED photopolymerization

From Table 3, it can be seen that most of the pyrylium salts have an absorption band in UV-Visible range. Recent works have shown that pyrylium compounds can be used to initiate a dual-cure polymerization. Indeed, these molecules, especially **TPP**, are able to cure cationically an epoxide resin by photopolymerization and thermal

Table 3. Validation of method B1LYP/6-311+G** with polarizable continuum model calculation (PCM) for computation of singlet transition energy of pyrylium compounds with experimental data.

| Pyrylium salts | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   |
|----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Experiment in eV (in nm) | 3.06 (405) | 3.19 (389) | 3.19 (389) | 3.79 (327) | 3.60 (344) | 2.63 (471) | 2.97 (417) | 3.11 (399) | 2.71 (458) |
|                  | 3.49 (355) | Overlapped | 4.52 (274) | 4.05 (306) | 5.08 (244) | 3.31 (374) | 3.42 (363) | 3.52 (352) | 3.02 (410) |
|                  | 4.47 (277) | 4.52 (274) |     |     |     | 3.89 (319) | 4.33 (286) | 4.49 (276) | 4.08 (304) |
|                  |     |     |     |     |     | 4.49 (276) |     | 4.61 (268) |     |
| Computed in eV (in nm) | 3.11 (398) | 3.36 (369) | 3.24 (383) | 3.78 (328) | 3.63 (342) | 2.70 (459) | 2.96 (419) | 2.96 (419) | 2.74 (452) |
|                  | 3.45 (359) | 3.79 (327) | 4.48 (276) | 4.56 (272) | 4.92 (252) | 3.26 (380) | 3.24 (382) | 3.24 (383) | 3.00 (413) |
|                  | 4.44 (279) | 4.95 (250) |     |     |     | 3.80 (326) | 4.27 (290) | 4.27 (290) | 4.06 (305) |
|                  |     |     |     |     |     | 4.31 (287) |     | 4.51 (275) |     |
| Errors in eV (in nm) | 0.05 (7) | 0.17 (20) | 0.05 (6) | 0.01 (1) | 0.03 (2) | 0.07 (12) | 0.01 (2) | 0.15 (20) | 0.03 (6) |
|                  | 0.04 (4) | 0.04 (2) | 0.51 (34) | 0.16 (8) |     | 0.05 (4) | 0.18 (19) | 0.28 (36) | 0.02 (3) |
|                  | 0.03 (2) | 0.43 (24) |     |     |     | 0.09 (7) | 0.06 (4) | 0.22 (14) | 0.02 (1) |
|                  |     |     |     |     |     | 0.18 (11) |     | 0.1 (7) |     |

Average error 0.12 eV / 10 nm
polymerization.

A cycloaliphatic diepoxide (Genomer 7210, Rahn) containing 3 wt% of TPP⁺ dissolved in propylene carbonate (1:4 ratio) was used to perform some photopolymerization experiments. The sample was irradiated under UV light (Hg-Xe with a reflector at 365nm and irradiance around 70 mW/cm²).

![Fig. 4. Photopolymerization experiments by RT-FTIR of an cycloaliphatic diepoxy in presence of TPP⁺ and under different irradiation source.](image)

The same experiment was done using a LED at 395nm with similar irradiation (Fig. 4). Both experiments, followed by real-time FTIR, show a fast polymerization under UV (365nm) and visible light (395nm). With the target is to develop a dual-cure process under LED, this result is promising.

3.3. Dual-cure process under 395 nm LED

It has been established that TPP⁺ is an efficient cationic photo and thermal initiator [1-4]. Thus, it is a quite suitable compound for designing a dual-cure initiating system. As said before, in such case, the photopolymerization reaction occurs at the irradiated surface and prompts the thermal reaction in depth. Therefore, a front of polymerization propagates from the irradiated side to the bulk. To achieve such process, the heat released by photochemical process must perfectly match with heat required to initiate thermal polymerization.

In the case of TPP⁺, the heat released by the thermal process may be increased by using a coinitiator. It was reported that hydrogen peroxide at 1 mol% is sufficient to induce a front of polymerization [3]. It has been also shown that at 3 wt% of isobutylvinylether can be use in addition to an oxetane monomer to speed up the thermal polymerization of the epoxy resin [1].

As discussed before, the photopolymerization could be carried out under visible light. As the efficiency of photopolymerization under LED was lower than under UV light, the irradiation power and coinitiator concentration were adapted to obtain a front of polymerization. The results are presented in Fig. 5 using 1 wt% of hydrogen peroxide or 3 wt% of isobutylvinylether. These two experiments show the possibility to perform a photoinduced thermal frontal polymerization under LED at 395nm. The thermal waves move down through the sample from the surface (0 mm) to depth (3 cm) with an average velocity of 1.1 cm/min for hydrogen peroxide and 2.6 cm/min for isobutylvinylether. It can be noticed that the front temperature is stable, meaning that the fronts have reached a stable regime until the end of the sample. Interestingly, the plots of velocity front vs. depth show a curvature and tend to increase in depth. This fact is related to the concentration of coinitiator. Indeed, high concentration of coinitiator decreases the pot life of the formulation. Therefore, the sample slowly polymerizes in depth while the front of polymerization moves from the surface. Thus, energy required to support the front of polymerization is decreasing in depth, leading to a raise of the velocity. This effect could be a great advantage when the formulation contains fillers to promote the displacement of the front.

4. Conclusion

The UV-visible absorption spectra of new photo-thermal cationic initiators such as pyrylium salts can be predicted using Density Functional theory. B1LYP/6-311+G** with PCM calculation appear as the most suitable computation method. The absorption in the visible range of pyrylium salts allows the photopolymerization of epoxy resins under 395 nm LED. More interestingly, the surface photopolymerization with the LED was used to prompt a thermal polymerization of the resin in depth through a photoinduced thermal frontal polymerization process. This open the opportunity to develop new initiating systems for photoinduced polymerization of thick and filled epoxy resins.

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Fig. 5. Dual-cure experiments under LED (395 nm, 900mW/cm², 1 min). (a) TPP 3wt% / H₂O₂ 1wt% / GENOMER 7210; (b) TPP 3wt% / IBVE 3wt% / (GENOMER 7210/OXT 101, 25/75).

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