

Photoinitiator Byproducts: All You've Wanted to Know (and Never Asked)

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In recent years, Lamberti has been working on a particular class of photoinitiators called difunctional. They have several positive characteristics that led us to their further study and development. The most fundamental and interesting advantage is that the byproducts developed during the photocuring process minimize the unwanted characteristics of monofunctional photoinitiators (such as migration of the parent compounds and of their photodecomposition derivatives). With these improvements, we can now prepare low-migration formulations that are particularly suitable for food packaging applications. In this work we will discuss the byproducts resulting from the photolysis of these products.

The difunctional photoinitiators discussed in this work are from different chemical classes, and are well-characterized molecules that show a high photoreactivity such that, despite their higher molecular weight, they can be added at the same weight percentages in the formulations as the lower molecular weight monofunctional photoinitiators. The photolysis byproducts of these photoinitiators are well-known and easily detectable. Moreover, these photoinitiators are easy-to-handle as they are supplied in a powder form. Three main Lamberti photoinitiators belong to this class—LFC 1861 (Type I photoinitiator), LFC 1001 (Type II photoinitiator) and

LFC 2098 (coinitiator). Each has its own peculiar characteristics and is suitable for particular applications.

Byproducts

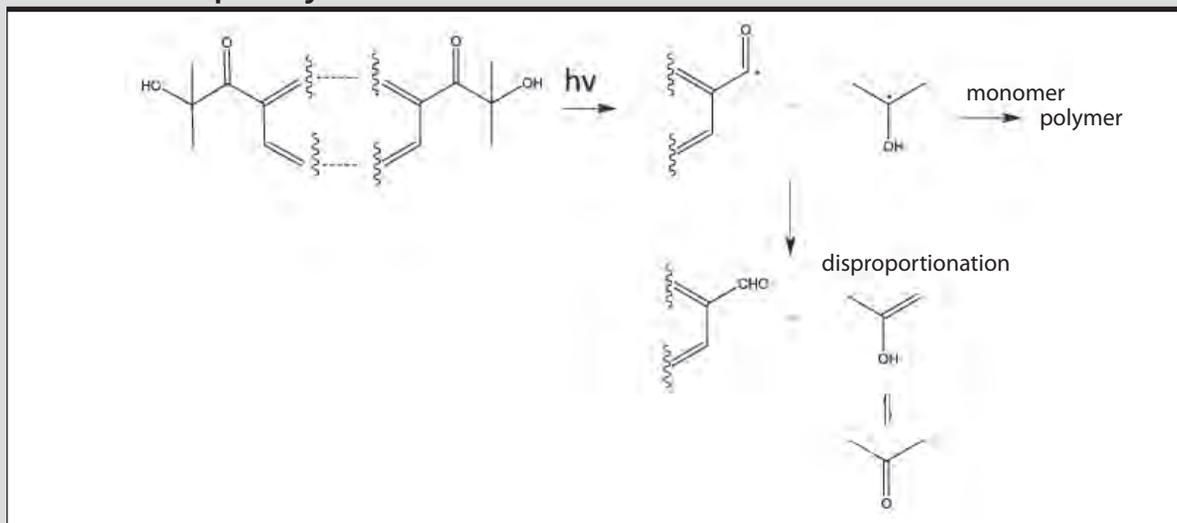
With UV technology, we know that the photoinitiators are generally assumed to create unknown or out-of-control byproducts. Because photoinitiators do develop byproducts, we wanted to show in this study that the byproducts developed under UV lamps are both well-known and detectable. This would further assert that UV technology is safe when the correct photoinitiators are properly investigated, formulated, applied and used. As it relates to food packaging, since only products that are detectable in the simulating fluids are relevant, this study deals only with stable byproducts developed after curing. The ones that can be recognized only by means of a radical scavenger are not taken into account.

Mechanism—LFC 1861

LFC 1861 is one of Lamberti's most important and performing products. It is a difunctional, oligomeric alpha-hydroxy ketone and is suitable for the most common UV lamps. It is largely used in many different fields of application such as graphic arts, coatings for electronics and enhancing performance in food packaging. On March 7, 2008, LFC 1861 was approved by the FDA for direct contact with

FIGURE 1

Mechanism of photolysis of LFC 1861



foodstuff (FCN 772). The mechanism of photolysis of α -hydroxy-ketones is well-known.¹ See Figure 1.

Photolysis—LFC 1861

To demonstrate that LFC 1861 reacts with the same mechanism, a photolysis experiment was carried out in CH_3CN (0.02M Hg lamp, 80W/cm, 10' exposure) and the following products were isolated as shown in Figure 2.

The structures I, II and III were assigned as the stable photolysis products that were isolated by liquid chromatography (SiO_2 , eluent $\text{CH}_2\text{Cl}_2/$

MeOH 95/5) analyzed by ^1H NMR and HPLC-MS. Compounds I, II and III demonstrated that LFC 1861, when exposed to UV light, reacts with the same mechanism of a common α -hydroxy-ketone. All byproducts were synthesized and the retention time was determined by high-performance liquid chromatography (HPLC).

Migration Test—LFC 1861

The migration test was carried out to verify the presence of the photoinitiator itself and the byproducts I, II and III in the simulating fluids.

Formulation and Migration Conditions—Direct Contact

To carry out the trials, a clear formulation photoinitiated with 4% of LFC 1861 was used. The formulation is applied with a thickness of 6 g/m^2 on aluminum foil. The samples were cured with Fusion equipment with a medium-pressure Hg lamp. Power of the lamp was 160 W/cm. Belt speed was 15 m/min.

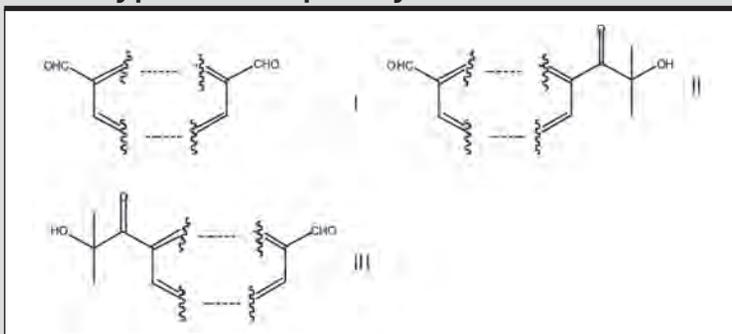
From the cured foils were cut three samples of 6.45 cm^2 each. The samples prepared were put into 10 ml of simulating fluids—EtOH 10% or EtOH 95%—according to European Food Safety Authority (EFSA) Guidelines that requests the ratio surface/volume between 0.5 and 2. The samples were exposed for 10 days at 40°C and then cooled at room temperature. The simulating fluids were analyzed by HPLC (See Table 1).

Mechanism—LFC 1001 and LFC 2098

LFC 1001 is a difunctional photoinitiator characterized by a ketosulphone moiety and a phenyl-ketone moiety. A coinitiator is needed

FIGURE 2

Stable byproducts of photolysis of LFC 1861



to obtain the best performance of LFC 1001. Its absorption spectrum is suitable for the most common UV lamps. It develops low odor after curing and has low migration and low extraction properties. This makes LFC 1001 a very interesting product to be used in food packaging applications. It is designed mainly for dark inks, but it is used in different application fields such as graphic arts and clear coatings.

The suggested cointiator used with LFC 1001 to optimize its performance is LFC 2098. It is a difunctional, high-molecular weight amine cointiator, suitable for conventional UV lamps. It is characterized by high reactivity, low yellowing and low odor properties. It also shows (in combination with LFC 1001) very low migration in a variety of simulating fluids. See Figure 3.

TABLE 1

LFC 1861 migration results in EtOH 10% and EtOH 95%

Products	EtOH 10% 10 days, 40°C	EtOH 95% 10 days, 40°C
LFC 1861	udl*	udl*
I	udl*	udl*
II	udl*	udl*
III	udl*	udl*

*udl = under detection limits

FIGURE 3

Structure of LFC 1001

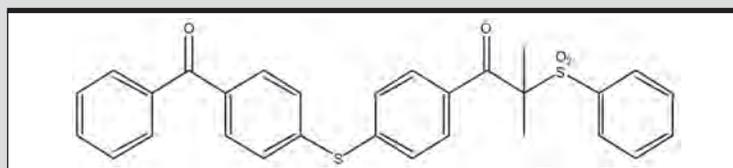


FIGURE 4

Ketosulphone photolysis

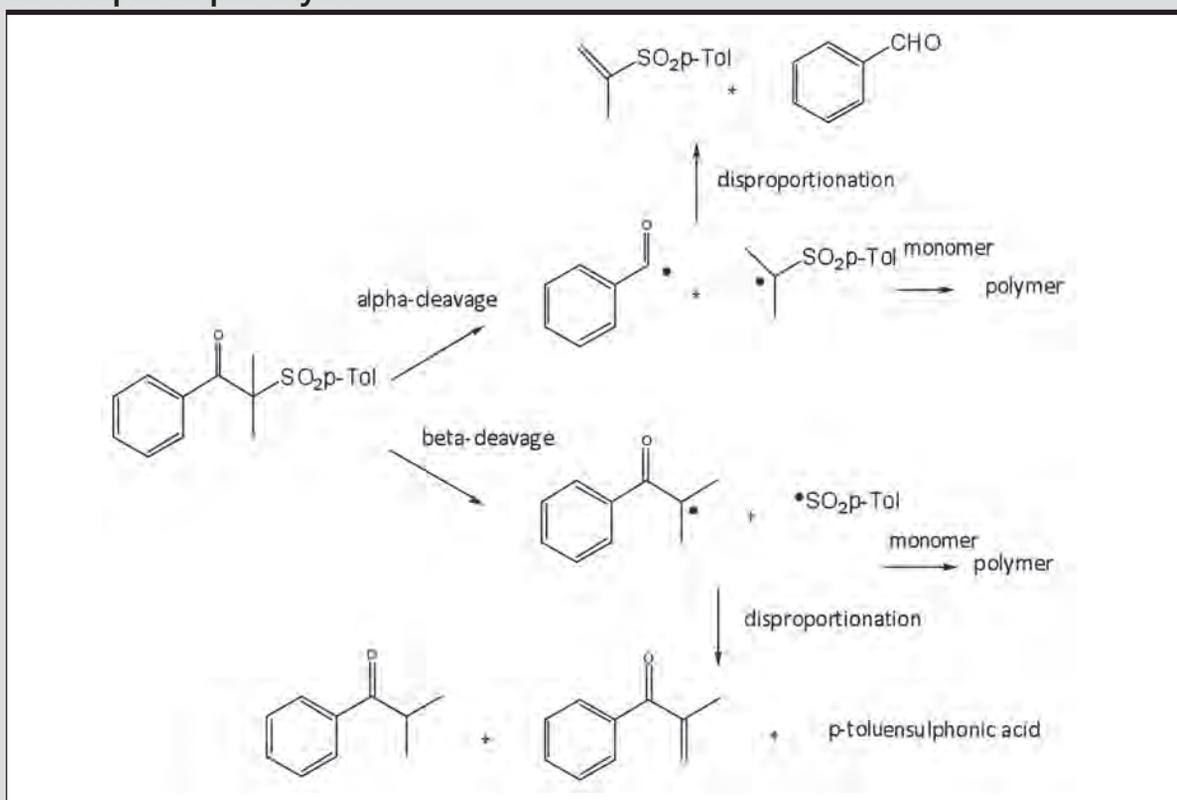
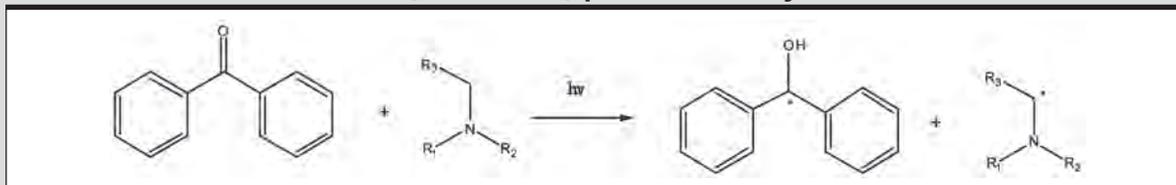


FIGURE 5

Aromatic ketone and amine (coinitiator) photoreactivity



According to the literature,^{2,3} the α and β -cleavage of the ketosulphone generate radicals able to activate a polymerization with acrylic systems. These radicals can also generate more stable products. Regarding the other photosensitive part of the molecule, the aromatic ketone, a coinitiator is needed to generate a reactive radical to start the polymerization. The mechanism, as reported in literature,⁴ is shown in Figure 4.

In the case of Figure 5, the radical of the amine promotes the polymerization and the ketyl radical dimerizes.

Photolysis—LFC 1001 and LFC 2098

To investigate the mechanism of generation of radicals, a photolysis has been carried out in CH₃CN with LFC 1001 (0.01M), LFC 2098 (0.01M) Hg lamp, 125W/cm, 30' exposure. After irradiation, CH₃CN was evaporated and the products were isolated by liquid chromatography (SiO₂, toluene/CH₃COOEt = 9/1 then CH₃Cl/MeOH = 9/1) and analyzed by H¹NMR and HPLC-MS. Stable products were isolated as shown Figure 6.

Structures IV and V in Figure 6 come from the fragmentation of the β -ketosulphone. These byproducts were synthesized and the retention time was determined by HPLC.

Migration Test—LFC 1001 and LFC 2098

The migration tests were carried out to verify the presence of the photoinitiator and coinitiator itself and the byproducts IV and V in the simulating fluids.

Formulation and Migration Conditions—Indirect Contact

The formulation used for the test is a laboratory blue ink photoinitiated with 3% of LFC 1001 and 3% of LFC 2098. The formulation was applied using an IGT-C1 applier with a thickness of 3 g/m² on cardboard. The samples were cured with Fusion equipment with a medium-pressure Hg lamp. Power of the lamp was 160 W/cm. Belt speed was 30 m/min.

To obtain the “reverse side conditions,” the cured side of the cardboard was put in contact with

a new cardboard and put under a pressure of 20 kg for 10 days at room temperature. From the noncured foils were cut three samples of 6.45 cm² each. The samples prepared were put into 10 ml of simulating fluids—EtOH 10% or EtOH 95%—according to EFSA guidelines that requests the ratio surface/volume between 0.5 and 2.

The samples were exposed for 10 days at 40°C and then cooled at room temperature. The simulating fluids were analyzed by HPLC. See Table 2.

Conclusion

With this study, we demonstrated that difunctional photoinitiators are totally under control. We precisely know which are the stable byproducts that photoinitiators develop after curing; can synthesize and detect them; and also verify the presence in the simulating fluids of the migration test thanks to modern analytical methods. The direct result is that all the risks are minimized and the UV technology can be considered safe for

FIGURE 6

Stable byproducts of photolysis of LFC 1001 and LFC 2098



a very challenging field of application such as food packaging. ▶

References

1. K. K. Dietliker, "Photoinitiators for Free Radical and Cationic Polymerization" in Chemistry e technology of UV & EB formulations for coatings, inks and paints, Vol. 3, page 129.
2. K. K. Dietliker, "Photoinitiators for Free Radical and Cationic Polymerization" in Chemistry e technology of UV & EB formulations for coatings, inks and paints, Vol. 3, page 188.
3. J. P. Fouassier, "Photoinitiation, Photopolymerization and Photocuring," page 29.
4. K. K. Dietliker, "Photoinitiators for Free Radical and Cationic Polymerization" in Chemistry e technology of UV & EB formulations for coatings, inks and paints, Vol. 3, page 193.

TABLE 2

LFC 1001 and LFC 2098 migration test results in EtOH 10% and EtOH 95%

Products	EtOH 10% 10 days, 40°C	EtOH 95% 10 days, 40°C
LFC 1001	udl*	udl*
LFC 2098	udl*	udl*
IV	udl*	udl*
V	udl*	udl*

*udl = under detection limits

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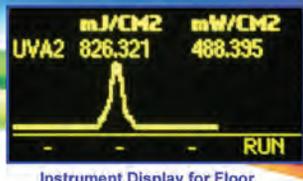
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PROFILER PUCKS

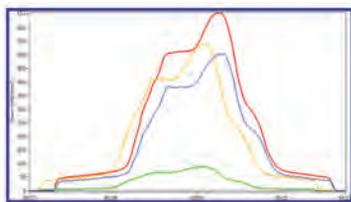
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 - ◆ Generate customized templates for user notes
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Instrument Display for Floor



	Sample File	Reference File	Difference
UVA - Power (mW/cm2)	1550.406	325.695	1224.711
Power (%)	376.0	0	376.0
Energy (mJ/cm2)	346.611	373.638	(26.827)
Energy (%)	(7.2)	0	(7.2)
UVB - Power (mW/cm2)	586.618	317.299	269.318
Power (%)	84.9	0	84.9
Energy (mJ/cm2)	91.949	348.207	(256.258)
Energy (%)	(73.6)	0	(73.6)



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