Second generation 3-Ketocoumarin: oligomeric and zero migration photoinitiators for LED curing

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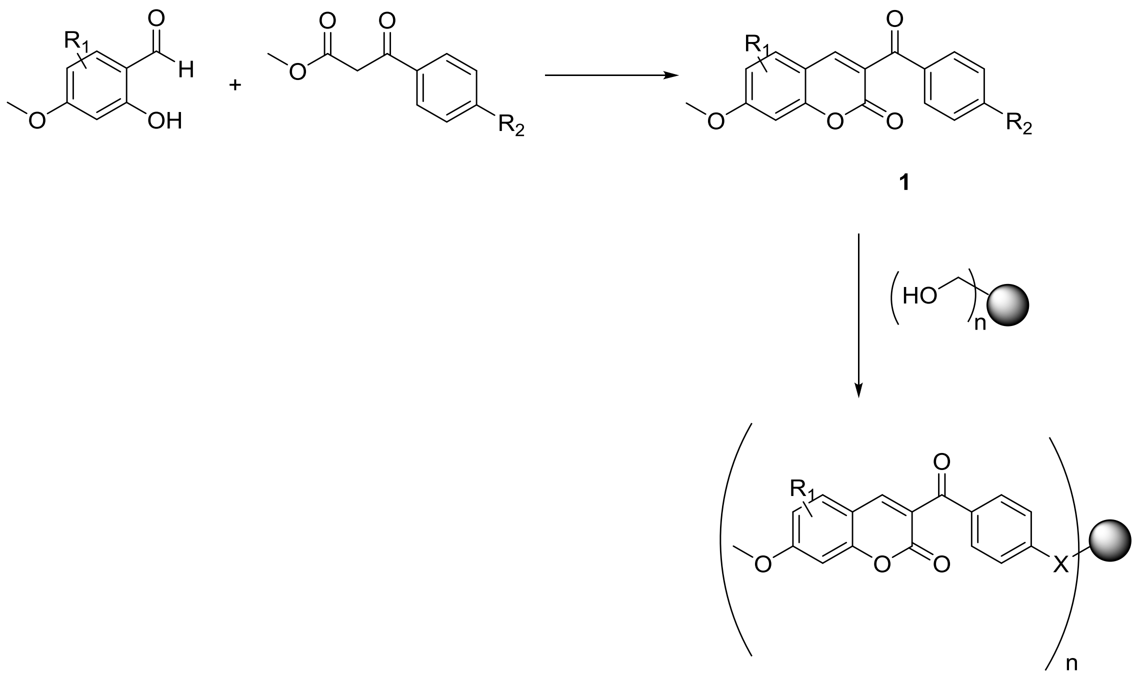
Abstract
Two years ago at RadTech 2016, IGM presented on novel ketocomarin photoinitiator chemistry. Now, following the launch of a first generation low migration ketocoumarin photoinitiator for LED cure (385/395 nm) for wood coatings and graphic arts, we will present further patented exploitations of this Type II photoinitiator type, with the objective of reaching a zero migration low yellowing system for multiple end uses in inks and coatings, particularly wood coatings. We will present structural chemistry, scientific and applications data to underline the novelty and utility of this chemistry.

Introduction
3-ketocoumarins are known from '80s, they were first used[1] for the sensitization of photocrosslinkable polymers, such as poly(vinyl cinnamate).
Depending on the structure, 3-ketocoumarins have absorption maxima between 330 and 450 nm[2] and the proper combination with a suitable coinitiator provides highly reactive photoinitiating system. 3-ketocoumarins bearing at least one alkoxy substitution have absorption maxima around 360 nm leading them particularly suitable for LED applications. Unfortunately, the 3-ketocoumarins suffer of poor solubility in all acrylic monomers, which means that it is very hard to formulate such compounds in acceptable loading in almost all formulations.
In our previous work[3], we developed a new 3-ketocoumarin (Esacure 3644) highly soluble and highly reactive at LED wavelengths, one of the main characteristic was the low yellowing compared to ITX. Close to the high reactivity and low yellowing, Esacure 3644 showed also a low migration profile in all preliminary tests even if its molecular weight was close to 500 Da. As described in literature[4], increasing the molecular weight towards 1000 Da lead to practically zero migration.
Currently the class of molecules known to give the best performances in migration conditions are the polymeric photoinitiators and the acrylated photoinitiators, these two classes were extensively explored in the last years. At the moment, the only polymeric/oligomeric photoinitiators for LED at 395 nm are the polymeric thioxanthone (e.g. Omnipol TX) and the polymeric acylphosphine oxide (Omnipol TP), while in the acrylated class there is only the acrylated thioxanthone (Omnipol 3TX).
Therefore, our efforts in the last years were in developing a novel class of oligomeric 3-ketocumarins able to reach the limit of zero migration, we decide to explore both classes, oligomeric 3-ketocoumarins and oligomeric acrylated 3-ketocoumarins.
The novel 3-ketocoumarins are especially suited in graphic arts (e.g. inkjet, offset, flexo and screen inks, overprint varnishes), 3D printing, medical applications, wood coatings, glass coatings, adhesives and electronics.

Results and Discussion

Synthesis

The novel 3-ketocoumarins were synthesized in a multistep synthesis, the key intermediate was prepared by the condensation of the corresponding salicylaldehyde with the β-ketoesters.

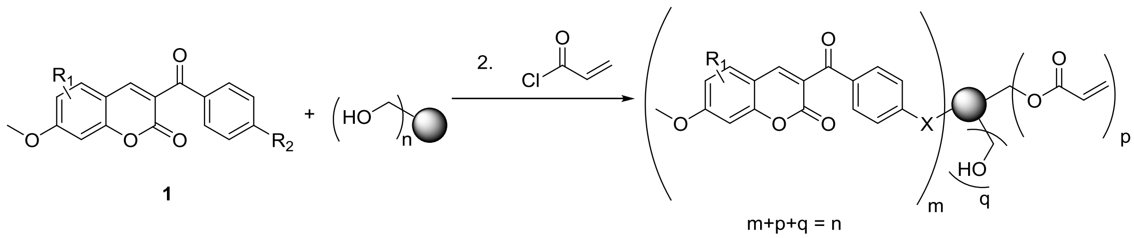


The intermediate **1** can be linked to different polyol to give a series of oligomeric 3-ketocoumarins with MW ranging from about 1000 Da to 3000 Da and with different PI loading, depending on the polyol (see Table 1).

Compound	Number of core functionalities
LFC3806	3
LFC3809	3
LFC3811	6
LFC3812	4
LFC3823	3

Table 1. Oligomeric 3-ketocoumarins.

The oligomeric acrylated 3-ketocoumarins were synthesized starting from the intermediate **1** by reaction with different polyol and then with the acryloyl chloride, the PI loading and double bond content are shown in Table 2.



Compound	Number of core functionalities	% acrylic function	% 3-ketocoumarin
LFC3820	3	40	40
LFC3822	4	33	50
LFC3826	6	28	67
LFC3827	4	38	25
LFC3829	3	27	50
LFC3830	3	50	50

Table 2. Oligomeric acrylated 3-ketocoumarins.

UV-Vis Spectra

The novel oligomeric and oligomeric acrylated 3-ketocoumarins show absorption spectra with a maximum at about 360 nm in acetonitrile. As an example is reported the absorption spectra of LFC3806, at three concentrations 0.1%, 0.01% and 0.001% w/w, wearing the same chromophore the absorption spectra of all the other compounds is very similar. From Figure 1, it is clear that the absorption pattern of the novel PIs perfectly fits with LED wavelengths (365 nm, 385 nm and 395 nm).

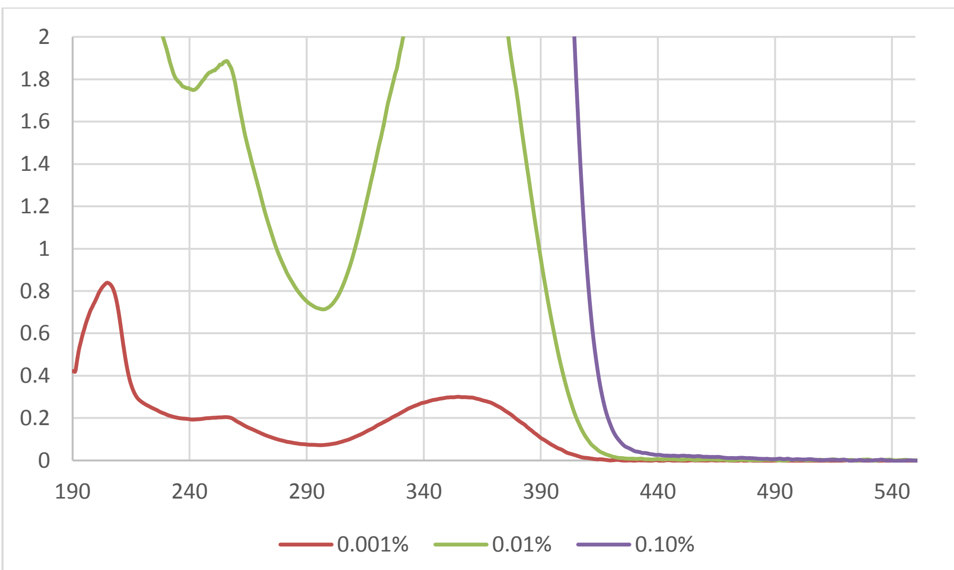


Figure 1. LFC3806 UV-Vis Spectra in Acetonitrile.

UV-LED Curing Tests

The first test for the evaluation of the new oligomeric 3-ketocoumarins reactivity was performed by the measure of the double bonds conversion (1407 and 810 cm^{-1}) by FT-IR in a clear coating.

The photopolymerizable compositions for the test were prepared dissolving the photoinitiator and the coinitiator (Ethyl-4-dimethylamino benzoate, EDB) at a concentration of 3 % by weight each in a mixture 99.5:0.5 wt of bisphenol A epoxy diacrylate and silicone diacrylate. The LED source used was an LX400+ system equipped with a UVLED spot centered at 400nm (Excelitas).

Isopropyl Thioxanthone (ITX), Esacure 3644 and Omnipol TX were used as reference.

We also measured the reactivity of these molecules in a cyan ink for inkjet printing, the concentration of the photoinitiator and the coinitiator was 5% by weight each (Figure 2b).

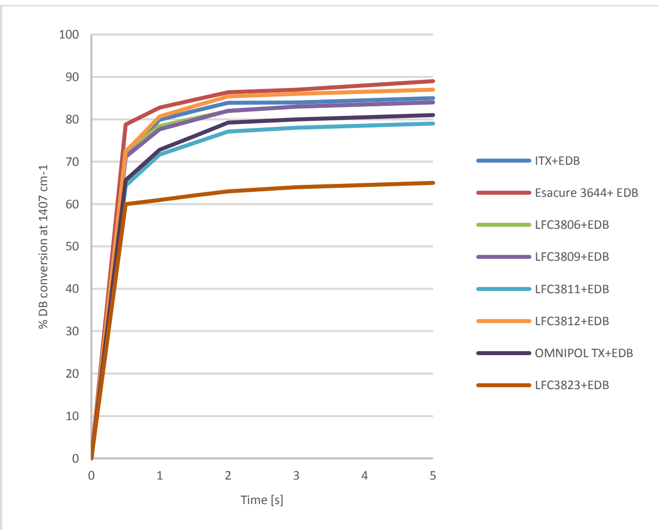


Figure 2a. FT-IR at 400nm in clear coating. Conditions: PE substrate, 6μm thickness, under air.

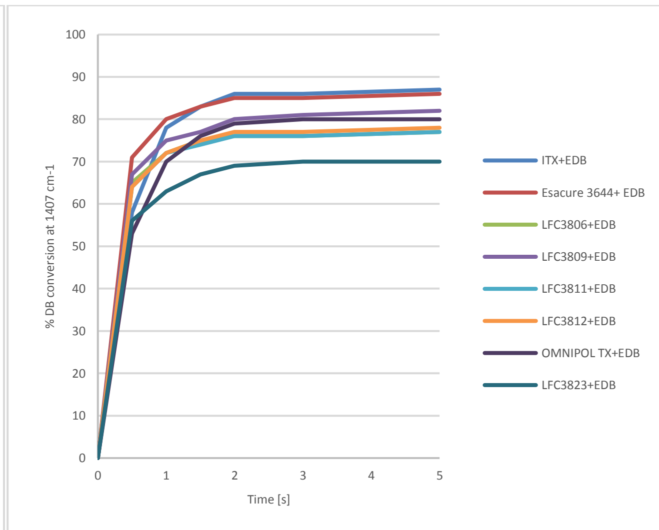


Figure 2b: FT-IR at 400nm in cyan inkjet ink. Conditions: PE substrate, 12μm thickness, under air.

From Figure 2a, we can observe that in clear formulation, the reactivity of LFC3806, LFC3809 and LFC3812 is very close to that of ITX and superior to Omnipol TX. The less reactive compound instead is LFC3823.

In pigmented system, the highest values of conversion are reached by Esacure 3644 and ITX, but the trifunctional oligomeric 3-ketocoumarins (LFC3806 and LFC3809) shows a reactivity comparable to Omnipol TX.

From Figure 2a and 2b, it is clear that 3-ketocoumarins LFC3806 and LFC3809 are the most reactive.

The same screening tests were performed on the oligomeric acrylated 3-ketocoumarins see Figure 3a and 3b.

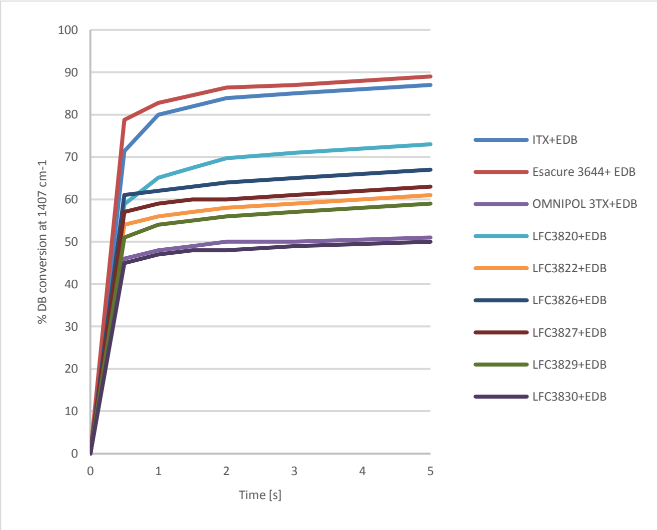


Figure 3a. FT-IR at 400nm in clear coating. Conditions: PE substrate, 6µm thickness, under air.

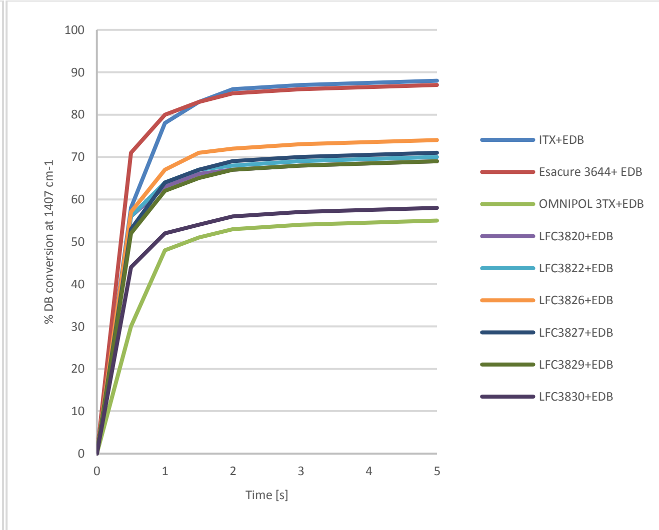


Figure 3b: FT-IR at 400nm in cyan inkjet ink. Conditions: PE substrate, 12µm thickness, under air.

From Figure 3a, we can observe that the reactivity of Esacure 3644 and ITX is higher than the acrylated photoinitiators, but the reactivity of the novel oligomeric acrylated 3-ketocoumarins is always superior to Omnipol 3TX. The best performances were obtained with LFC3820 and LFC3822.

Therefore, the oligomeric 3-ketocoumarins LFC3806, LFC3809, LFC3820 and LFC3822 were further evaluated.

Tack-free measurement in a clear system were performed with Hg lamp and LED lamp at 395 nm (Figure 4a and 4b), the concentration of PI and coinitiator (Esacure A198) is 3% each by weight. Three coinitiators were used in order to evaluate the differences in reactivity and yellowing.

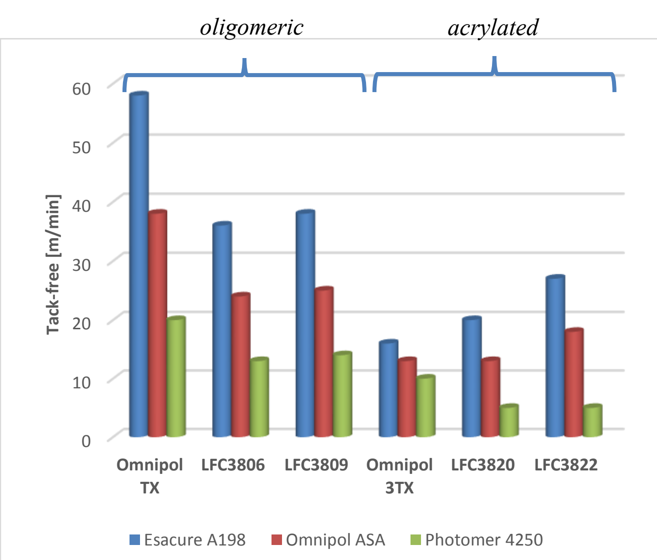


Figure 4a. Tack-free in clear coating (Hg Lamp 120W/cm). Conditions: cardboard, 6µm thickness, under air.

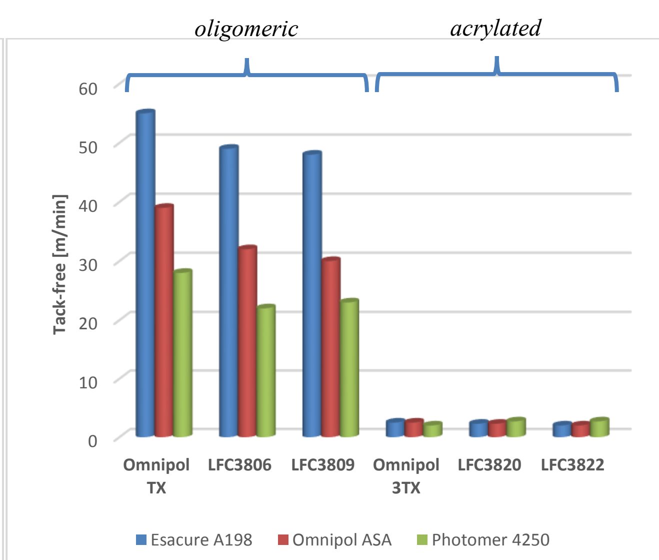


Figure 4b: Tack-free in clear coating (LED 395 nm 16W/cm). Conditions: cardboard, 6µm thickness, under air.

In Figure 4a and 4b, the best performances are obtain with aromatic amines and the reactivity depends on coinitiator structure: aromatic amine -single molecule (Esacure A198)> polymeric aromatic amine (Omnipol ASA)> acrylated amine (Photomer 4250).
Under Hg lamp irradiation the most reactive compound is Omnipol TX, although the novel 3-ketocoumarins are always more reactive than Omnipol 3TX. Under LED lamp, instead, the reactivity of the oligomeric 3-ketocoumarins (LFC3806 and LFC3809) is very close to Omnipol TX, while the reactivity of all acrylated compounds is very poor.
The color stability was evaluated by a color guide BYK 45/0. The results are summarized in Figure 5a and 5b.

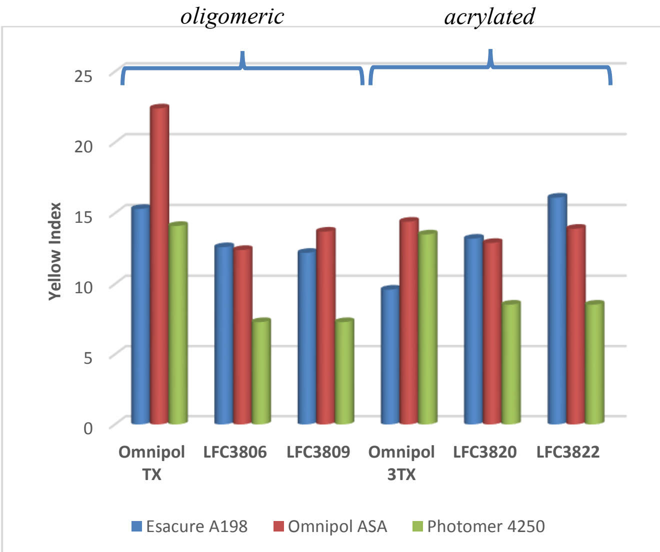


Figure 5a. Yellow Index in clear coating (Hg Lamp 120W/cm). Conditions: cardboard, 6μm thickness, under air.

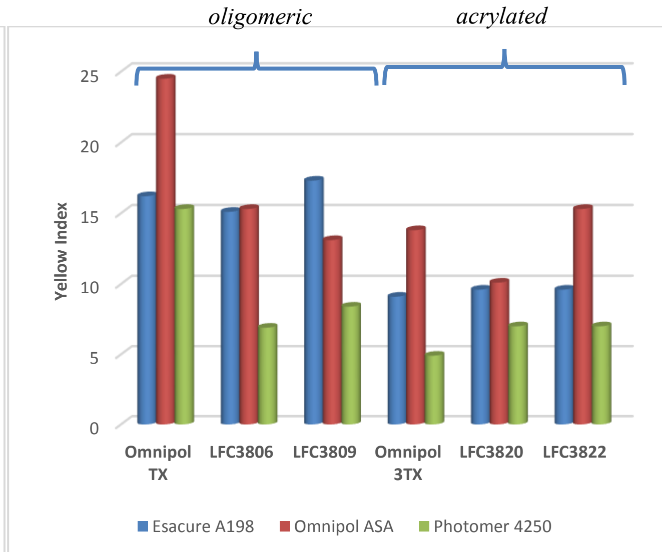


Figure 5b: Yellow Index in clear coating (LED 395 nm 16W/cm). Conditions: cardboard, 6μm thickness, under air.

All 3-ketocoumarin compounds show a Yellow Index lower than Omnipol TX with all coinitiators. The best results are reached when the acrylated coinitiator (Photomer 4250) is used; in this case the Yellow Index in more than 50% lower.

Through cure measures were performed at 395nm (16W and 4W) in an industrial cyan offset ink and in a cyan inkjet ink (Figure 6 and 7).
The solutions of photoinitiator and coinitiator were prepared at a concentration of 3% (offset ink) and 6% (inkjet ink) by weight each.

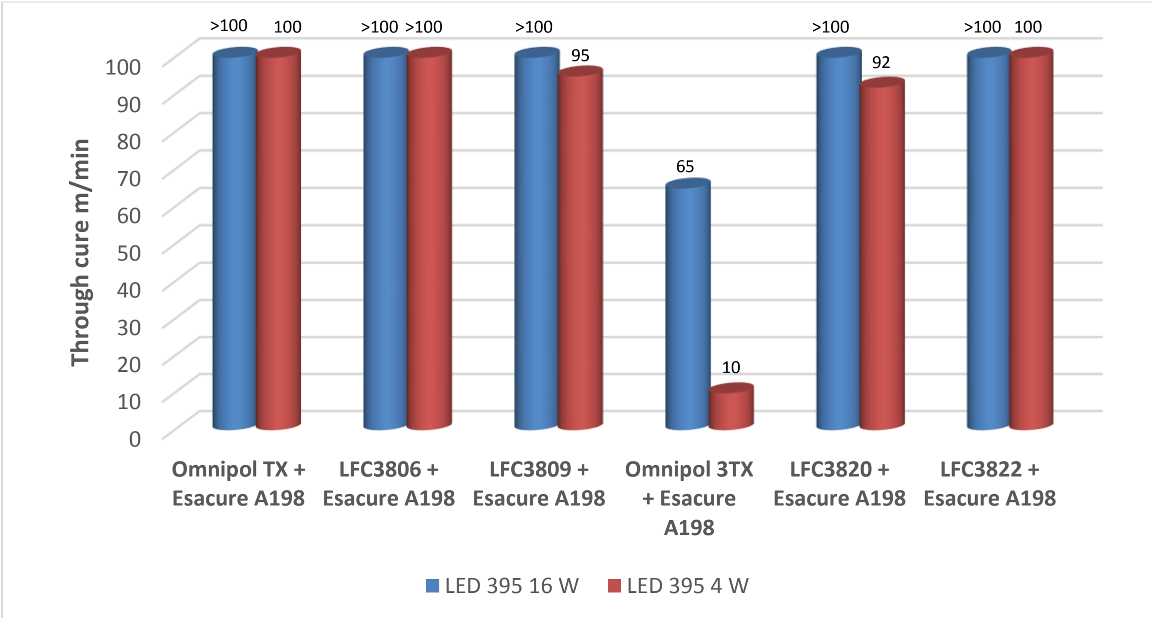


Figure 6. Through cure measurement at 395 nm in industrial cyan offset ink. Conditions: cartonboard, 1.5 µm thickness.

In the industrial offset ink, with the 395nm LED lamp at 16W the novel oligomeric and acrylated 3-ketocoumarins show the same reactivity of Omnipol TX, but when we reduce the power of the lamp at 4W, LFC3806 (oligomeric) results as the best compound, more reactive than Omnipol TX. The other three compounds show a reactivity very close to Omnipol TX and much higher than Omnipol 3TX (Figure 6).

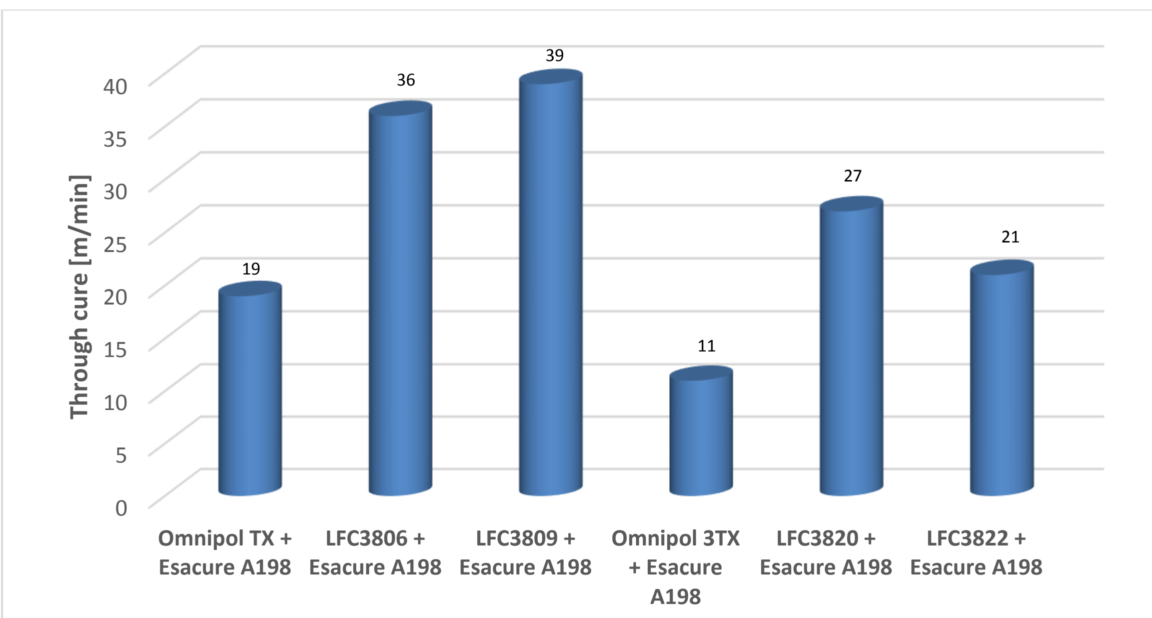


Figure 7. Through cure measurement at 395 nm (16W/cm) in cyan inkjet ink. Conditions: cartonboard, 6µm thickness.

In the cyan inkjet ink the 3-ketocoumarins showed their best performance, both oligomeric and oligomeric acrylated are always more reactive than the two reference compounds (Omnipol TX and Omnipol 3TX).

The best result are reached from LFC3809 that is twice faster than Omnipol TX and more than 3 times faster than Omnipol 3TX. Also, the oligomeric acrylated 3-ketocoumarins show a very good performance, LFC3820 is 50% more reactive than Omnipol TX and 2.5 times faster than Omnipol 3TX.
These results confirm the excellent performance of the novel 3-ketocoumarins in pigmented systems.

Migration tests
Even if, all novel oligomeric and oligomeric acrylated 3-ketocoumarins show a molecular weight higher than 1000 Da, so their migration is zero and 3-ketocoumarins are type II photoinitiators, so they do not generate any break down product during irradiation; a preliminary test to verify the ability of LFC3820 and LFC3806 to migrate or to be extracted after curing was made.
The radiation curable compositions for the test were prepared according to Table 3. The weight % was based on the total weight of the radiation curable composition.

	COMP-1	**COMP-2**
LFC3820	0.5	
LFC3806	-	0.5
Omnipol ASA	0.5	0.5
Photomer 4600	1.0	1.0
VEEA	4.0	4.0
Photomer 280	0.03	0.03

Table 3. Photocurable compositions for preliminary migration studies.

The radiation curable composition COMP-1, COMP-2 were coated on a PE substrate using a bar coater and a 10 μm wired bar. Each coated sample was cured with Hg lamp (240 W) and an LED lamp 395nm (16 W/cm^2). The curing speed is shown in Table 4.

	Curing Speed Hg lamp (240W) m/min	**Curing Speed LED lamp 395nm (16W/cm^2) m/min**
COMP-1	25	10 (2pass)
COMP-2	35	10

Table 4. Curing speed of photocutrable compositions.

The samples of 1 inch^2 of COMP-1 and COMP-2 were put into a 50ml beacker and extracted with 4.5 ml acetonitrile, using ultrasound for 30 minutes. The extract was transferred into a flask and adjusted to 5 ml. The solutions was injected on the HPLC and no residue of LFC3806 and LFC3820 was detectable. This means that the novel photoinitiators are completely built into the network.

Conclusions

We developed two novel classes of 3-ketocoumarins with a good reactivity and low yellowing compared to commercial photoinitiators, the high molecular weight, which guarantees a zero migration profile, did not affect the reactivity. In particular in pigmented systems, the novel compounds showed excellent performance.

The most promising compound is LFC3806, its high PIs loading and the relatively small core guarantee a very good performance in all tests and in particular, in pigmented systems; the absence of free double bonds seems to be more promising in terms of long-term stability.

[1] D. P. Specht, P. A. Martic and S. Farid *Tetrahedron* **38**, 1203 (1982)
[2] A. Bernini Freddi, M. Morone, G. Norcini *Design of new 3-ketocoumarins for UV LED curing* Radtech USA (2016)
[3] A. Bernini Freddi, M. Morone, G. Norcini *WO2017216699* (2017)
[4] W. A. Green *Industrial Photoinitiators* p. 93 CRC Press (2010)