First author:

Dr. Peter Eladio Ludwig, Laboratory Manager Specialty Chemicals,
Schmid Rhyner AG, www.schmid-rhyner.ch

+41 79 516 02 71, p.ludwig@schmid-rhyner.ch, Soodring 29, 8134 Adliswil

Second author:

Dr. Alexander Johannes Oßenbach, Manager Specialty Chemicals
Schmid Rhyner AG, www.schmid-rhyner.ch

+41 44 712 62 74, a.ossenbach@schmid-rhyner.ch, Soodring 29, 8134 Adliswil

Third author:

Baktash Jahanbani, Laboratory Technician Basic Development
Schmid Rhyner AG, www.schmid-rhyner.ch

+41 79 557 67 61, b.jahanbani@schmid-rhyner.ch, Soodring 29, 8134 Adliswil

Next Generation Low Migration Photoinitiators:

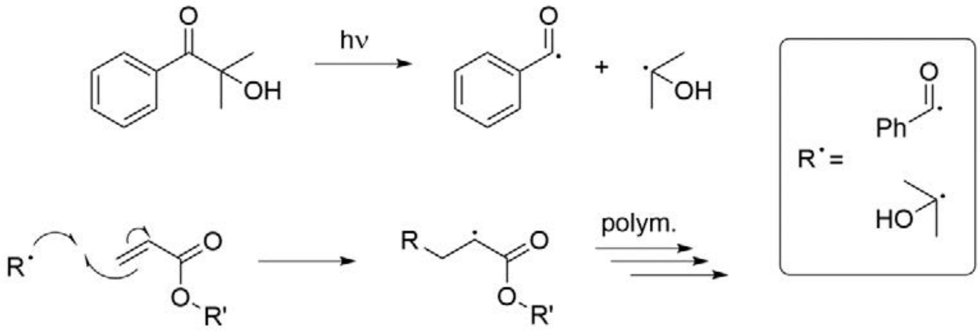
Tethered Type II Photoinitiators for Food Packaging Applications

INTRODUCTION

Printed materials such as commercial printing or packaging material nowadays widely use radically curing UV technology. The advantage of fast processing times and the possibility for immediate post-processing results in shorter turnaround times and therefore in improved efficiency for the printers. In addition UV coatings as a top layer improve the scuff-resistance and make the surface less susceptible against moisture, grease and solvents.

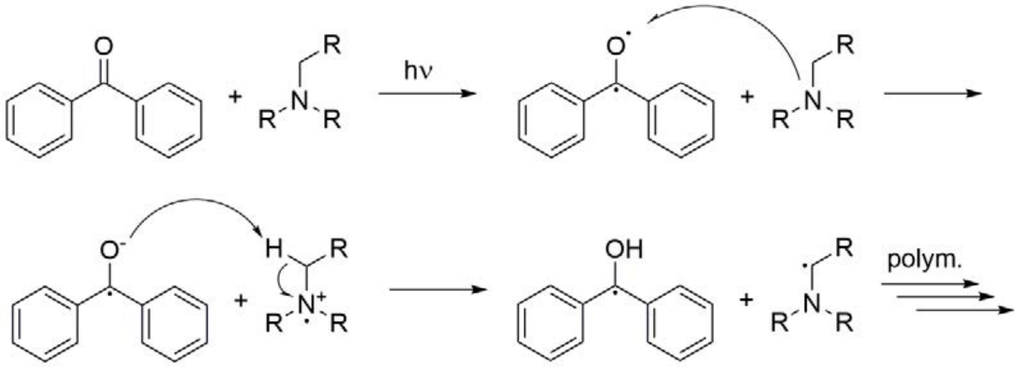
Besides for the technical benefits UV coatings are often used to improve the appearance of a printed article with high gloss or matt effects applied as a full coverage or as a spot to highlight certain elements for improved visibility, e.g., a point of sale or in an advertising magazine. Recent developments even enable the printers to introduce haptic effects with UV coatings. Relief coatings in which raised structures are printed are meanwhile well known in the industry. However, a rough sand touch, a moist looking and feeling wet touch or a smooth soft touch coating give brand owners the opportunity to design packaging solutions with higher brand recognition as the touch sense increases the recognition value. [1] Especially in high competition markets, such as food packaging brand recognition is an important factor. Although the above mentioned applications are not critical in standard commercial printing, their use in food packaging or other sensitive packaging applications challenges the ink and coating formulators. Particular measures need to be taken in order to protect the packed goods from coating or ink components migrating from the packaging. This requires that the converter controls the degree of curing which depends on the press speed as well as the UV lamps' condition. In addition the formulator may chose ingredients for such coatings or inks that are less prone to migrate. Among the various components of UV curing inks or coatings that need to be monitored concerning their risk of migration and contamination of food stuff are photoinitiators, which gained public attention with e.g., the detection of isopropylthioxanthone (ITX) photoinitiator in baby milk in 2005. [2] Although photoinitiators are inevitable in UV curing formulations, special care has to be taken in the selection process of a suitable photoinitiator for a specific application.

Photoinitiators used in today's printing inks and coatings comprise mainly two groups. Type I photoinitiators decompose upon UV irradiation homolytic in two radicals which directly initiate the radical chain reaction (*cf.* Scheme 1). Typical representatives are e.g., acetophenone derivatives and in particular α–hydroxyl– and α–aminoacetophenones along with acylphosphine oxides.



Scheme 1: Photoinitiation mechanism of type I photoinitiators

Type II photoinitiators on the other hand essentially are photosensitisers, usually bearing a benzophenone or thioxanthone moiety as a chromophore. By absorbing UV light the chromophore is excited into a triplet state, which by itself is not reactive enough to initiate a radical polymerization. If no synergist, such as a tertiary amine, is present the triplet state would decay into the ground state yielding the initial molecule. In the presence of an amine, an electron transfer from the nitrogen followed by a proton abstraction can take place forming an α–aminoalkyl radical which is reactive enough to initiate a chain polymerisation (*cf.* Scheme 2).

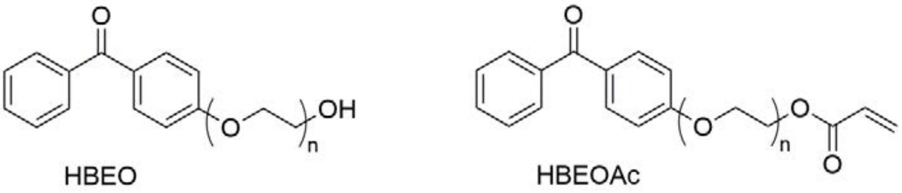


Scheme 2: Co-initiation mechanism of type II photoinitiators

As a result the degradation products [3] [4] [5] of the type II photoinitiator as well as residual photoinitiator (that either did not get excited or that's triplet state decayed or got quenched) remain in the cured film posing a risk for migration. There are different approaches by the industry to minimize the migration potential. A major impact on the mobility and hence migration potential of substances is the molecular weight. Aparicio und M. Elizalde calculated that molecular weights below 300 g/mol significantly increase diffusion coefficients [6] and therefore are more likely to migrate. Thus, photoinitiator suppliers often increase molecular weight by tethering two or more photosensitive moieties together, usually achieving in type II photoinitiators an average molecular weight of 650-1000 g/mol, often referred as oligomeric or polymeric photoinitiators. The EFSA published that molecular weights above 1000 g/mol are considered as not toxicologically relevant. Although many of such commercially available photoinitiators do not fulfil this non-toxicological requirement they have a significantly reduced migration potential and are successfully used in many applications. Higher molecular weight structures typically come along with an increased viscosity of the photoinitiator itself or the final formulation which makes them challenging to use in low viscous applications e.g., in inkjet inks and coatings.

ACRYLIC TETHERED PHOTOINITIATOR

A potential approach to minimise migration of type II photoinitiators while keeping a low viscosity could be to keep the average molecular weight low and introduce a radically polymerisable unit. Thus the photoinitiator can be covalently bound into the polymer network of the cured film and hence the potential for migration should be minimised e.g., in case of the recently commercialised photoinitiator HBEOAc shown in Scheme 3.



Scheme 3: Structures of photoinitiators HBEO and HBEOAc

In this case a benzophenone moiety has been tethered to an acrylate moiety and thus can participate in the chain polymerisation with the (multifunctional) acrylates typically used in printing applications. Therefore, unreacted benzophenone moieties as well as potential degradation products can be covalently bound into the polymeric structure resulting in a significant decrease of their migration potential. In order to verify this theory, the migration potential was evaluated in a test formulation using commercially available compounds frequently used in printing inks for food packaging applications (*cf.* Table 1).

Substance	weight-%
Genomer 5161 (Rahn AG)	9.21
OTA-480 (Allnex)	55.25
Miramer M300 (Rahn AG)	27.62
Irgacure 127 (BASF)	0.92
Tego Rad 2011 (Evonik Industries)	0.46
Type II photoinitiator	6.54

Table 1: Composition of test formulation for the estimation of the migration potential

For a comparison of the migration potential a reference of the non-acrylated alcohol HBEO of the acrylic tethered photoinitiator HBEOAc (*cf.* Scheme 3) was analysed as well as were two commercially available oligomeric photoinitiators bearing a benzophenone moiety as chromophore. All photoinitiators are technical products with a molecular mass distribution. In case of PI 1 and PI 2 (*cf.* Table 2) the molar mass is between 650-1000 g/mol while the average molar mass of HBEOAc was determined to be 450 g/mol. From the available data it was estimated that the chromophore per mass content should be similar to each other. In direct comparison the HBEO has a slight smaller average molecular mass (400 g/mol) then HBEOAc resulting in slightly higher chromophore content of the final coating.

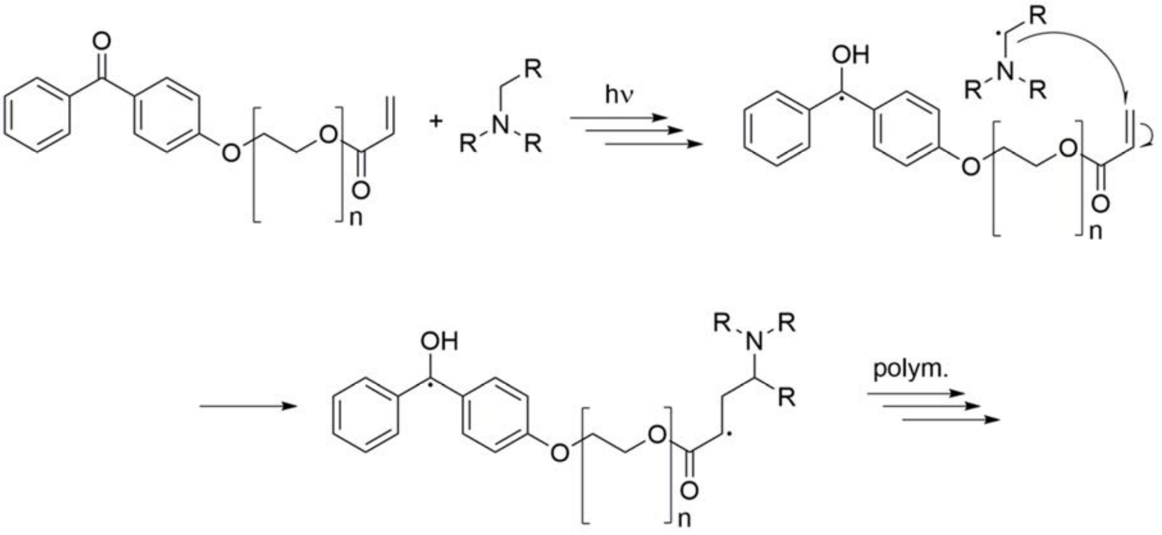
Varnishes 1-4 (*cf.* Table 2) were applied with a number 2 Mayer rod on a polyester substrate (Folex Folanorm 0.18mm) resulting in a film weight of about 10 g/m^2. The samples were passed under a UV Hg-lamp (200W/cm) at a band speed of 20 m/min. The curing was tested with a talcum test in which after the first pass half of the sample is covered with a carton and passed a second time under the UV light. The so prepared sample is sprinkled with talcum powder and carefully wiped clean with a cotton tissue. Given that the coating is not cured sufficiently the part which was irradiated once would exhibit a grey haze on the surface while the twice irradiated part should appear clear. The sample is considered cured at the tested speed if no difference between the once and twice irradiated sides is visible. All samples were assessed to be fully cured at the speed of 20 m/min.

The migration behaviour was tested by extracting 1dm^2 of the polyester samples with ethanol (95%) for 24h at room temperature. The samples were fully immersed. The ethanol was then analysed by LC/MS for extracted photoinitiator content in order to determine its residual content (*cf.* Table 2).

	Type II photoinitiator	Estimated average molecular weight	Viscosity according to manufacturer (25°C) Pa*s	Residual photoinitiator µg/dm^2
Varnish 1	PI 1	800-1000	100	50
Varnish 2	PI 2	800-1000	200	39
Varnish 3	HBEO	400	2.5	1445
Varnish 4	HBEOAc	450	1.1	10

Table 2: Photoinitiators used in test formulations to estimate migration potential

The extracted residual photoinitiator of oligomeric PI 1 and PI 2 were detected with 50 µg/dm^2 and 39 µg/dm^2 respectively. Assuming that their estimated molar mass range is similar; the extraction results show also similar behavior. The HBEO as a non-tethered photoinitiator showed with 1445 µg/dm^2 the highest amount of extractable substance congruous with the expectations. The residual amount of HBEOAc extracted out of varnish 4 was determined at 10 µg/dm^2. As postulated the acrylic group tethered to the photoinitiator decreased the amount of extractable material significantly showing a higher impact on immobilization than is achieved by increasing the molar mass. As the HBEOAc is only a monofunctional acrylate this seems like a remarkably low amount of extract in comparison to HBEO which has a similar molecular weight though shows a 140-fold amount of extract. The likelihood of a monofunctional acrylate to participate in the polymerisation process depends on the proximity of the acrylic group to the active chain end or to the initiating molecule. In case of HBEOAc the acrylic group is tethered to the chromophore, thus forcing the acrylic group in close proximity to an active chain end which was generated by its intramolecularly bound chromophore. Also a reaction with the activated synergist is very likely due to the proximity of all three reaction partners (*cf.* Scheme 4) resulting in a decreased migration potential.

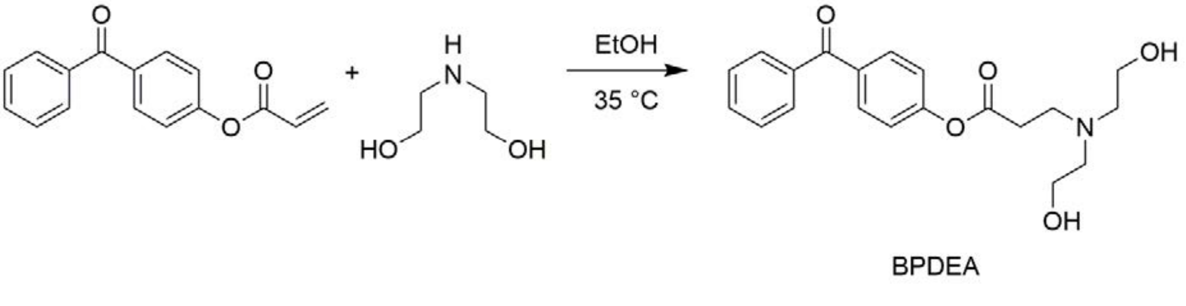


Scheme 4: Photoinitiation and polymerisation of HBEOAc

The actual impact of said geometry on the efficiency of the electron transfer and chain initiating process could not be determined in this experiment. However, if the photoinitiator would be tethered to an amine synergist instead of the acrylic function, the electron transfer from the synergist to the excited chromophore should be more efficient due to the close proximity thus the system might show a higher reactivity compared to an intermolecular mechanism.

AMINE TETHERED PHOTOINITIATORS

Given the apparent positive effect on network integration due to vicinity of the acrylate group to the photoactive centre as depicted in Scheme 4, it can be assumed that a functional group acting as synergist on that position would also benefit of such a vicinity effect. There has been work on that topic by Temel *et al.* [7] using an amine functionalised benzophenone called BPDEA (*cf.* Scheme 5).



Scheme 5: Synthesis of BPDEA

They found, that intermolecular co-initiation was more relevant in their system than intramolecular co-initiation. BPDEA though has a rather short tether of only four atoms length which lacks flexibility thus preventing a close interaction of the photosensitive moiety with the amine synergist. It can be assumed that the contribution of the intramolecular mechanism to the initiation step increases stepwise by elongation of the tether until a maximum efficacy is reached. Beyond that point the intramolecular contribution might decrease again due to the lowered probability of the amine moiety getting close to the chromophore. In an attempt to show that a positive effect of intramolecular co-initiation can be observed we synthesised a photoinitiator with a tether that has a polymeric distribution ranging between 7 and 22 bearing an amine at the end of the tether (BPtA). Said photoinitiator was compared regarding its reactivity to an equivalently tethered photoinitiator bearing an acrylic group (HBEOAc)[1] that is commercially available, as well as 4–Methylbenzophenone (4MBz). In order to compare the reactivity a varnish was formulated based on trifunctional acrylates containing 7% of the above mentioned photoinitiators and a total amount of 0.9%w/w of nitrogen (*cf.* Table 3), *i.e.*, that in case of BPtA we have a contribution of nitrogen from the photoinitiator to the varnish of 0.2%w/w of nitrogen and therefore, 0.7%w/w of nitrogen were added through another synergist. As amines do not solely act as co-initiator, but also prevent oxygen inhibition on the surface. Therefore further nitrogen addition through amines is necessary to create a realistic system for printing application.

	Varnish 5	Varnish 6	Varnish 7
Photoinitiator	BPtA	HBEOAc	4MBz
%w/w of N	0.9	0.9	0.9

Table 3: Photoinitiators used in varnishes for reactivity tests

The resulting varnishes were applied to a black cardboard using a number 1 Mayer rod resulting in a 6μm thick film, which was subsequently cured under UV light (100W/cm mercury lamp) at different speeds (30, 40, 50, 60, 70, 80 m/min). The curing degree was determined using the talcum test as described above with curing half of the surface a second time at 10 m/min to give a fully cured surface. The results of this reactivity test are summarised in Table 4.

Curing speed [m/min]	Varnish 5	Varnish 6	Varnish 7
30	1	1	1
40	1	1	1
50	1	2	1
60	1	3	1
70	2	4	2
80	3	4	3

Table 4: Degree of curing after first pass through UV lamp: 1=fully cured, 2=slight turbidity, 3=obvious turbidity, 4=tacky surface

As shown in Table 4 Varnish 5 containing BPtA performs equally to Varnish 7 which was formulated with 4MBz, while Varnish 6 shows a reduced reactivity. As there have been equivalent amounts of photoinitiator with regard to the total mass, this means that Varnish 5 and Varnish 6 have a lower chromophore content in regards to moles. As 4MBz has a molecular weight of 196.24 g/mol, while BPtA and HBEOAC due to their polymer distribution have an average molecular weight around 450 g/mol, this means that in fact Varnish 7 contains more than double the amount of chromophores than do Varnishes 5 & 6. This explains the reduced reactivity of Varnish 6. Varnish 5 shows a significantly increased reactivity apparently as a result of the intramolecular co-initiation mechanism.

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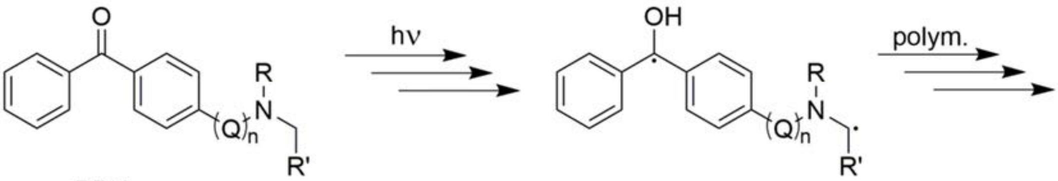
[1] Poly(oxy–1,2–ethanediyl)α–(1–oxo–2–propenyl)–ω–(4–benzoyl-phenoxy)–; CAS–No.: 478549-43-8

That would imply that a higher number of photoinitiators successfully initialise a polymerisation. Given that this initialisation is predominantly happening through an intramolecular mechanism, the photoinitiator would be integrated in the polymer matrix (*cf.* Scheme 6). In order to confirm these expectations migration tests with cured varnish films are planned.



BPtA
n = 7 – 22

Scheme 6: Intramolecular initiation mechanism of BPtA

SUMMARY

It could be shown, that tethering a benzophenone moiety to an acrylate results in a type II photoinitiator suitable for low migration formulations. The migration potential has been shown to be even lower than for polymeric type II photoinitiators. In addition the reduced viscosity of such a photoinitiator in comparison to polymeric photoinitiators leaves the formulator with more freedom to formulate. In a further experiment, it has been shown, that tethering a benzophenone to an amine creates a photoinitiator with a significantly increased reactivity in comparison to a benzophenone photoinitiator of comparable molecular weight. The reactivity is even increased to a point that it can compete with low molecular weight photoinitiators such as 4MBz. This suggests that an intramolecular initiation step is much more likely than an intermolecular one, which would result in the photoinitiator being integrated into the polymeric film. Migration tests are about to be performed, in order to confirm this theory.

ACKNOWLEDGEMENT

We thank Michael Kiehnel and Dr. Julia Volk from BCH Brühl for the support and cooperation on the work on acrylic tethered photoinitiators.

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Curricula

Peter E. Ludwig has studied chemistry at ETH Zürich and Imperial College London and received his PhD in Organometallic Chemistry from ETH Zurich. He has 3 years of experience in UV curing applications. Since 2015 he is working for Schmid Rhyner AG in Adliswil, Switzerland, where he currently holds the position as laboratory manager in specialty chemicals.

Dr. Alexander Ossenbach has studied Chemistry at Freie Universität Berlin and received his PhD in Polymer Chemistry from ETH Zurich. He has 7 years of experience in UV curing coatings, especially for food packaging applications and regulations. Currently responsible for Basic Development and Regulatory Affairs at Schmid Rhyner AG, Switzerland

Baktash Jahanbani has successfully completed his apprenticeship at F. Hoffmann-La Roche Ltd. as a Chemistry and pharmaceutical technologist with Federal Vocational Baccalaureate in Basel and received his diploma as a Senior Scientific Laboroatory Technician in 2017 from ABZ Zurich. He has 10 years of experience in UV curing applications. Curently he holds his position as a Laboratory Technician in Basic development at Schmid Rhyner AG, Switzerland