

# Advancements in Photolatent Amines: Expanding the Scope of Photolatent Base Technology

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## Introduction

Radiation curing is known since more than fifty years and has found a rapidly growing number of industrial applications since the mid 70ties. Using this ecologically benign technology, liquid high-solid formulations, which are stable over an extended time when stored under appropriate conditions in the dark, are transformed into cured products of high quality in a very fast process. These unique features allow the realization of considerable economic and ecological advantages. Light induced radically curing systems are nowadays well established and have enabled a wide variety of applications in coatings, graphic arts and electronic materials. Correspondingly, a wide variety of raw materials, including resin components<sup>1</sup> and photoinitiators<sup>2,3</sup> for radically curing formulations, are available.

Despite the obvious advantages of photoinduced radical curing, this technology has some limitations that are inherently linked to the radical crosslinking mechanism. These include oxygen inhibition, volume shrinkage or adhesion problems due to the ultrafast solidification process. Therefore, light triggered curing processes that maintain the advantages of radiation curing without suffering from these limitations could offer highly attractive solutions for certain applications. The search for such alternative light curing processes is thus an important topic for the further development of radiation curing.

The light induced cationic polymerization has been introduced with the development of onium salt initiators in the seventies. Use of photolatent acids became thus an alternative approach in radiation curing that principally does not suffer from some of the aforementioned limitations. Nevertheless, it has found much less use than radically curing formulations. This is partly due to a smaller choice of raw materials and photoinitiators<sup>4</sup> and the higher costs of high performance resin components.

The crosslinking of suitable formulations by base-catalyzed polymerization and polycondensation reactions is well known for use in conventional coating applications and is highly attractive for certain applications. A larger number of very different formulations are known that are suitable for a broad range of applications. Base-catalyzed crosslinking processes include for example the addition of polyols to polyisocyanate to give polyurethanes,<sup>5</sup> ring-opening of epoxide groups by nucleophiles such as amines, thiols, carboxylates or anhydrides<sup>6,7</sup> or the Michael reaction of acetoacetate or malonate group containing polyesters with acrylate oligomers.<sup>8,9</sup> Curing of epoxides by imidazole derivatives is an example of a base-catalyzed homopolymerization reaction.<sup>6</sup> With all systems, the addition of a base catalyst results in the immediate initiation of the crosslinking process, which limits its use to two-component formulations that have to be applied within a short time after mixing.

Thus, latent base catalysts are an attractive possibility to improve control over the curing process of such formulations while maintaining cure speed and the excellent properties of the cured article. Thermally blocked amine catalysts are known, but require high deblocking temperatures in order to achieve a

sufficient shelf. The use of light as the trigger is definitely more attractive in order to achieve optimum control over the curing process.

Somewhat surprisingly, only a few efforts to convert base-catalyzed formulations into radiation curable systems for use in coating applications have been reported so far. In fact, the use of a photobase in a technical application has not been reported before 1990, when a paper dealing with photoresist applications was published.<sup>7</sup> Although the steadily increasing number of reports on the use of photolabile bases shows a growing interest in this technology, most of the work is still focused on resists and microlithography. First coating applications have been reported in 1998,<sup>8-10</sup> but remained restricted to a limited number of exploratory systems.

One important reason for this is the lack of suitable photolabile base catalysts. Photolabile primary amines are well documented in the literature as protective groups in synthetic chemistry. The same photochemistry was used for technical applications of photolabile bases in resists<sup>10-13</sup> and also for the first coating applications, where photogenerated primary amines were used as crosslinkers for epoxides<sup>8,9,14</sup> or acrylates.<sup>15,16</sup> However, for such a process stoichiometric amounts of the crosslinker have to be generated by a photoreaction, which imposes severe restrictions on the scope of these processes and their energy efficiency.

Primary amines are not useful as catalysts for base-catalyzed addition or condensation reactions which usually require tertiary amine catalysts. The photogeneration of tertiary amines is considerably more challenging, and corresponding compounds are thus much less known in the literature.<sup>17-21</sup> This lack of suitable photocatalysts in a field expected to give room for a broad range of new radiation curing applications has prompted us to develop a novel technology platform based on photolabile tertiary amines. A first example of such a compound has recently been reported<sup>22,23</sup> and the successful launch of a UV-A curable car refinish coating<sup>24</sup> and a special adhesive<sup>25</sup> using this compound is a first proof for the practical viability of the photolabile base technology. These applications are based on the addition of thiols to isocyanates, and hence a photogenerated tertiary amine was found to be sufficiently active as a catalyst. This class of photolabile bases is limited to the use with crosslinking reactions that require the deprotonation of compounds of relatively high acidity, such as the reaction of epoxides with carboxylates.<sup>27</sup> For the further dissemination of this technology it is, however, necessary to have additional types of photolabile amines available, which expand the type of resins that can be cured.

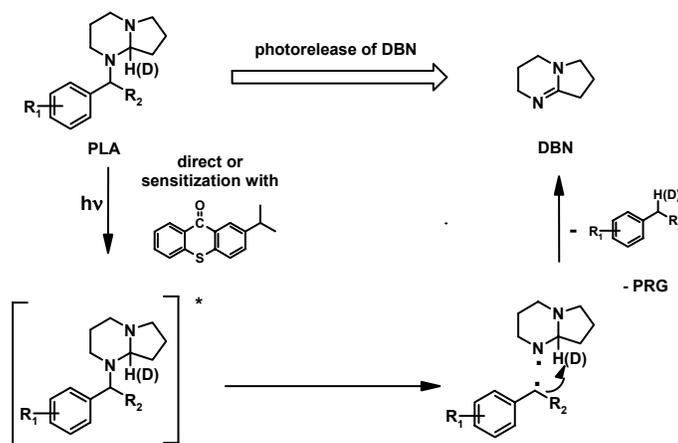
## **Development of a strong photolabile base catalyst**

Many base-catalyzed crosslinking reactions require amines with well balanced basicity and nucleophilicity properties. As an example, these factors and the steric hindrance strongly affect the efficiency of amine bases in isocyanate reactions.<sup>26</sup> The addition of weakly acidic acetoacetate or malonate derivatives to acrylic double bonds in a Michael addition reaction is efficiently catalyzed by amine bases such as tetramethyl guanidine (TMG), 1,5-diaza-bicyclo[4.3.0]non-5-ene (DBN) or 1,5-diazabicyclo[5.4.0]-undec-5-ene (DBU), but not by simple tertiary amines.<sup>28</sup> These amidine-type bases are in fact by 3-4 orders of magnitude more basic than tertiary amines (Table 1). Thus it was considered attractive to develop photolabile amines that produce an active catalyst providing the properties of an amidine base.

A challenge in the design of photolabile tertiary amine is the fact that the introduction of a photocleavable substituent on nitrogen results in the formation of ammonium salts. This concept has been used for most photolabile tertiary amines reported so far, but results in compounds with a correspondingly limited solubility and stability in formulations of low polarity and thus of limited practical use.

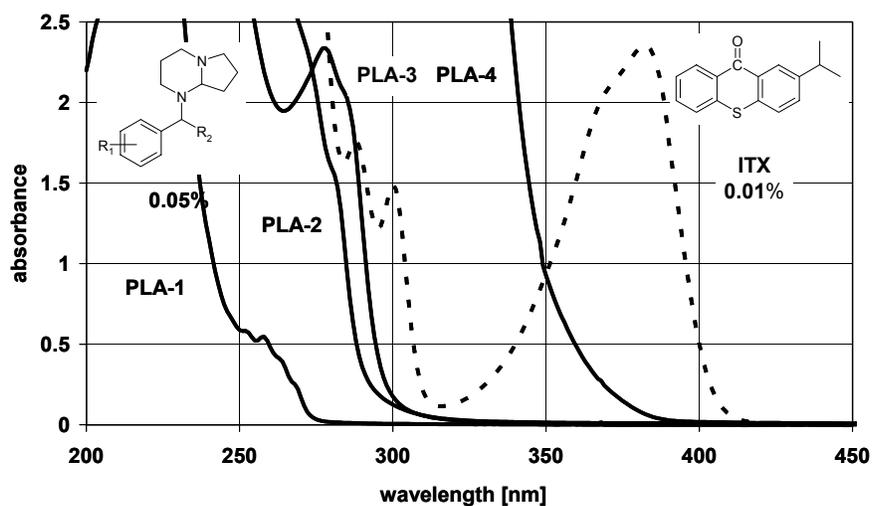


This hypothesis is supported by  $^1\text{H-NMR-CIDNP}$  studies showing emission type signal for the benzylic protons in the PRG group after the cleavage reaction, thereby supporting a radical precursor. Scrambling of deuterium from the aminal position in PLA to the PRG is also in agreement with the proposed mechanism. The radicals formed in this reaction are not efficient initiating species for radical reactions, since they are highly stabilized allyl or benzyl-type and non-reactive nitrogen-centered radicals.<sup>33</sup> These radicals preferentially undergo hydrogen abstraction reactions, which preferentially occur from a tertiary carbon atom in the amine cleavage product activated by the two amino substituents. This hydrogen transfer results in the regeneration of the amidine double bond in DBN.



**Figure 2.** Photorelease of DBN from N-benzylated precursors.

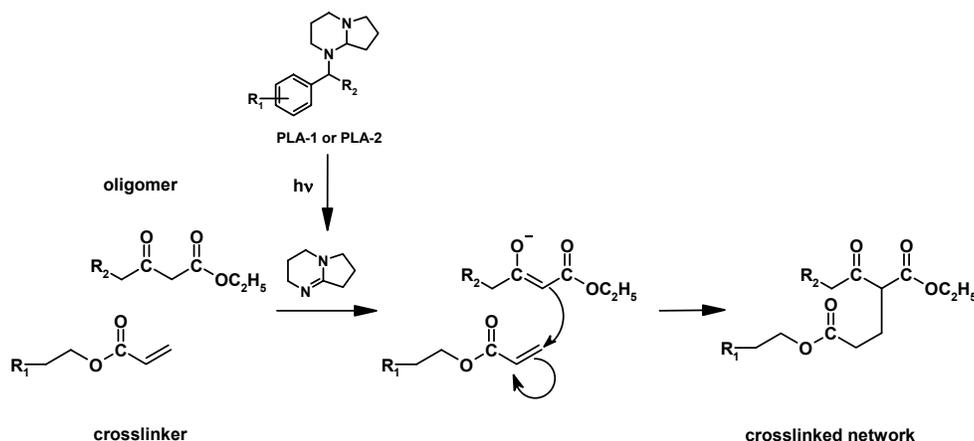
As expected, various properties of PLA can be optimized without affecting the active amine catalyst formed by a suitable design of the PRG in order to meet different requirements. As an example, the absorption spectra of these types of photolabile bases can be tuned over a wide range by changes in the substitution pattern on the benzylic moiety. The absorption spectra of four derivatives (PLA-1 - PLA-4) are shown in Figure 3.



**Figure 3.** Absorption spectra of PLA-1 - PLA-4 (continuous lines) and ITX (dotted line).

For practical applications, use of compounds PLA-1 or PLA-2, possessing an absorption that is limited to the UV-B spectral region, was found to be most useful both in view of the application properties and the synthetic access. The spectral sensitivity of these photolabile amines can easily be extended to longer wavelengths by the use of a sensitizer. In the course of an extensive evaluation, several types of aromatic ketones, such as substituted benzophenone derivatives or thioxanthenes, were found to be most useful as sensitizers. The combination of a photobase generator with a suitable sensitizer thus allows an easy tuning of the absorption characteristics of the initiating system to the requirements of the target application (Figure 3).

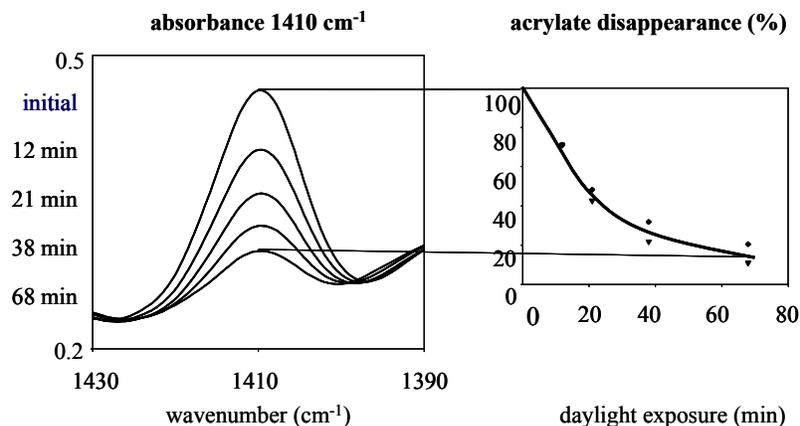
The photolabile DBN derivatives have been evaluated for the curing of a variety of different resins. The Michael addition of a CH-acidic acetoacetate or malonate functionality to acrylates acting as Michael acceptor is catalyzed by strong bases, and formulations based on this crosslinking chemistry have been known for a long time to give coatings of excellent quality.<sup>29,35</sup> Tack-free coatings are obtained in the presence of a catalyst such as DBN in less than one hour at room temperature. This feature limits the use of this system to 2K formulations with a relatively short pot life of the ready-to-use mixture.



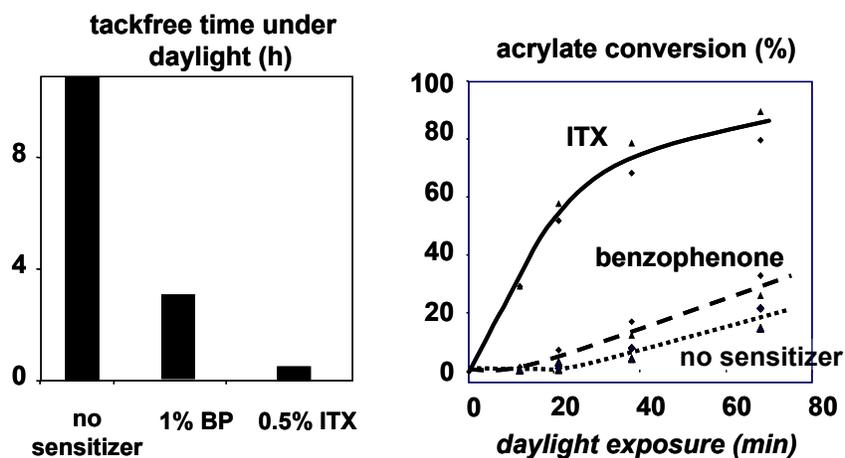
**Figure 4.** Crosslinking via Michael addition photoinduced by photolabile amines PLA-1 or PLA-2.

The use of the photolabile DBN allows the development of one-pack Michael formulations with a shelf life of up to one year (Figure 4). In fact, the latent catalyst, although still a tertiary amine, is not sufficiently basic to catalyze the Michael addition reaction.<sup>30</sup> Only when DBN is generated upon irradiation crosslinking is initiated, which then leads to tack-free coatings within a short time. The progress of this reaction can be followed by monitoring the decrease of the acrylate double bonds over time by measuring the absorbance of the C=C stretching band at 1410 cm<sup>-1</sup> in the IR spectrum. By this technique it could be demonstrated that using PLA-1 with ITX as sensitizer, approximately 80% of the acrylic double bonds have reacted within an hour upon irradiation with artificial daylight (Figure 5).

The acrylate conversion as observed by IR correlates well with the drying time of the coating measured by the Byk recorder. A comparison of the two methods using artificial daylight for curing is shown in Figure 6. As customary for such a curing mechanism, crosslinking continues after the switch-off of the light in the dark until the final full through-cure is achieved after several hours. For most applications, however, the achievement of a tack-free surface with no further dust uptake is considered crucial, and the time to achieve this state was thus used as measure for the performance of the photolabile amine.



**Figure 5.** Acrylate conversion in the photoinduced Michael reaction (monitoring by IR spectroscopy).

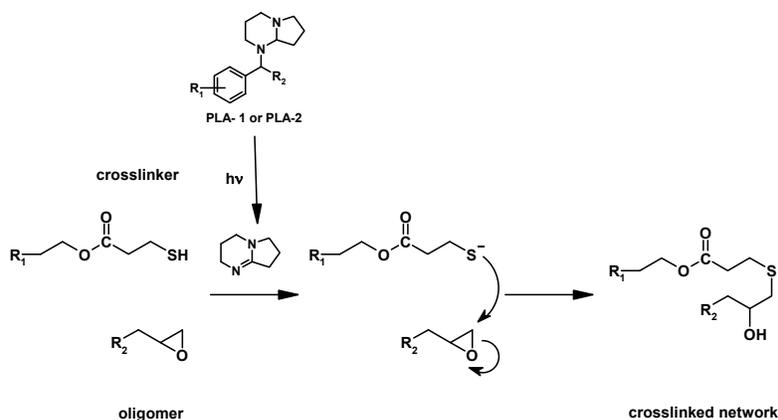


**Figure 6.** Comparison of drying time measured with the drying recorder from Byk-Gardner and acrylate conversion determined by IR spectroscopy. Concentration PLA-1: 2.5%

Since the photolatent base absorbs light only in the UV-B spectral region, no tack free coating is obtained even after eight hours of light exposure. This is confirmed by the low conversion of acrylate double bonds observed by RTIR analysis under the same conditions. Cure speed is significantly improved by the addition of a sensitizer with an absorption extending into the UV-A/visible range. Using ITX, a tack-free coating is obtained at room temperature in about 30 minutes, with a concomitant conversion of approximately 70% of the acrylic double bonds according to IR analysis.

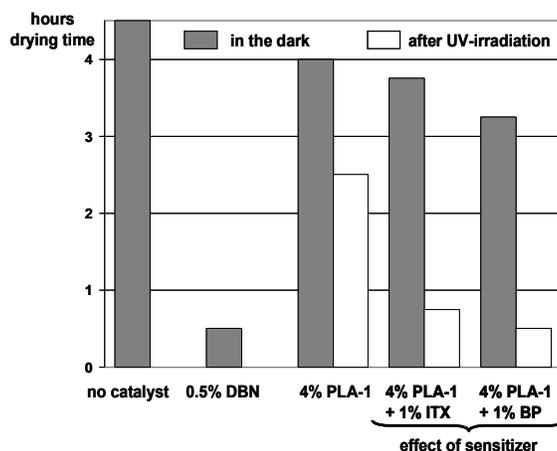
Thus, a one-pack formulation possessing a shelf life of several months in the dark and undergoing fast curing at room temperature upon irradiation with UV-A or daylight is obtained with the new photolatent amine PLA-1. Instead of  $\beta$ -keto esters or ketones as Michael donor components, it is also possible to use thiol-functionalized oligomers in a thiol/acrylate Michael formulation.

Another base-catalyzed crosslinking reaction is the ring-opening addition of thiols to epoxides (Figure 7). Such a formulation is stable at room temperature in the absence of a catalyst, but is cured within half an hour in the presence of 0.5% DBN. Addition of 4% of the photolatent amine PLA-1 results in a formulation with still has good shelf life stability in the dark. Irradiation with UV light gives a cured coating after 2.5 hours.



**Figure 7.** Crosslinking via thiol/epoxide addition reaction triggered by photolabile amines.

The curing of the system can again be significantly accelerated by the addition of a sensitizer. Interestingly, benzophenone is slightly more efficient than ITX when UV light of a mercury lamp is used for curing. The same cure speed as with unblocked DBN (Figure 8) can be achieved under these conditions. As usual in radiation curing applications, a careful optimization of the sensitizer/photolabile catalyst pair as well as of the concentration of the two components has to be established depending on the formulation and curing conditions in order to achieve the best results.

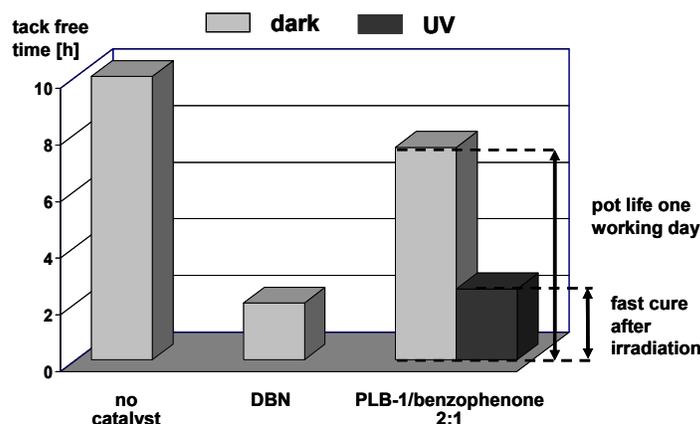


**Figure 8.** Drying time (hours) of an epoxide/thiol based formulation measured with the drying recorder from Byk-Gardner.

The curing of polyurethane resins is another attractive application for photolabile amines. Since polyols and isocyanates undergo a slow addition reaction even in the absence of a catalyst, such formulations are usually handled as 2K systems. As for all 2K systems, key for a flexible and efficient system with a broad application spectrum is an optimum balance between sufficient pot life of the “ready-to-use” formulation and fast cure speed after application of the lacquer. The use of a photolabile amine catalyst is an elegant solution to this problem. The latent form provides a relatively long pot life of the formulation after mixing of all components. After application of the coating, the catalyst is activated by light inducing fast curing at low temperature.

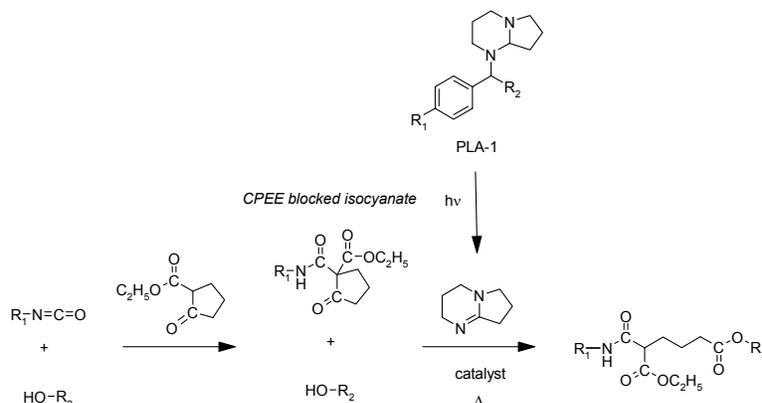
DBN is known to be a suitable catalyst for the alcohol/isocyanate addition reaction. Therefore, the new photolabile bases were also evaluated in this application. As expected, a potlife considerably longer than with free DBN is achieved when a photolabile amine such as PLA-1 is used. Since the pot-

life not only depends on the catalyst, but also on the type of isocyanate and alcohol used, a careful optimization of the formulation is required for an optimum balance between pot life and curing efficiency. Under optimized conditions, “ready-to-use” formulations that can be applied during one working day without losses due to premature gelation can thus be achieved. A tack-free coating is subsequently achieved after irradiation at room temperature within a time frame that is similar to that observed using unblocked DBN as catalyst (Figure 9). As for other applications, the use of a sensitizer is recommended in order to achieve the best match of the lamp emission with the absorbance of the initiating system.



**Figure 9.** Curing of a 2K polyurethane formulation containing 4% PLA-1/2% benzophenone. Curing conditions: 2x80W/cm mercury medium pressure lamp, cure speed 5m/min; drying time (hours) measured with the drying recorder from Byk-Gardner.

The use of blocked isocyanates allows the formulation of one pack systems with an extended shelf life. Most blocking concepts rely on the reversible addition of a suitable reagent to the isocyanate group. The disadvantage of these systems is the release of one equivalent of the blocking agent during the curing process at elevated temperatures, which may be a concern if the compound is volatile. Recently a novel concept of non-emissive blocking agents using cyclopentanone 2-carboxyethyl ester (CPEE) as blocking agent has been introduced.<sup>36</sup> Since the concept of non-emissive blocking agents is in line with the environmentally friendly radiation curing technology, it was of interest to check if one pack formulations using this blocking system can be cured with the photolabile bases PLA-1 or PLA-2. In fact it could be shown that a combination of both concepts is possible, allowing the formulation of one pack formulations that can be efficiently cured after irradiation (Figure 10).



**Figure 10.** Curing of a CPEE blocked polyisocyanate/polyol formulation using PLA-1 as photolabile catalyst.

Other applications of photolatent DBN are currently under investigation by us and others<sup>37</sup> and are proof of the increasing interest into applications of photolatent amines. The results of the extended evaluation of these compounds demonstrate the potential of this novel technology platform to extend radiation curing into new applications. The chemistry of the crosslinking reactions in these formulations is inherently slower than that of radically curing formulations. The photolatent base technology can therefore not compete for cure speed. However, resin chemistries hitherto not available for radiation curing can be used under well controlled curing conditions, giving access to products possessing new properties. Moreover, the unique curing properties allow the development of novel application techniques which may for example comprise additional process steps between activation and curing of the formulation.<sup>38,39</sup> The new technology is thus clearly complementary to existing radiation curing applications.

## Conclusions

The development of new photolatent amines that release amidine-type catalysts opens new opportunities for radiation curing, allowing the light-triggered curing of formulations catalyzed by strong DBN-type bases. Depending on the crosslinking chemistry involved, different application modes are possible. Components that react slowly even in the absence of a catalyst have to be used as two-component formulations, but significantly improved balance between a long potlife and fast curing provide considerable advantages for the end user in the form of easier handling, less losses and a higher through put. Other resin systems that do not react in the absence of a base catalyst can be handled as one-pot systems, with a shelf life of several months in the dark and fast cure on demand after irradiation. The use of sensitizers has proven to be a useful tool for the optimization of the light sensitivity to the irradiation conditions.

Since a variety of other base curable resins are known, new applications will arise in near future. Depending on the crosslinking mechanism and the application conditions, the careful selection of a photolatent base producing an appropriate catalyst is crucial for efficient curing. Research on photolatent bases is continuing, aiming at further expanding the scope of this new technology platform that is complementary to the existing UV-curing processes and opens new possibilities for radiation curing.

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