Photolatent Amines: New Opportunities in Radiation Curing

K. Dietliker, T. Jung, J. Benkhoff

Ciba Specialty Chemicals Inc., Schwarzwaldallee 215, CH-4002 Basel, Switzerland

Abstract

New concepts for photolatent amines have been developed, which allow the efficient phototriggered release of tertiary amines or amidine-type bases. In contrast to most photobase generators reported so far, the amines thus obtained are capable to act as catalysts for base-catalyzed crosslinking reactions. The energy-efficient radiation curing of various types of formulations that were so far not accessible for this technology becomes thus possible, as it is demonstrated for a two-component polyurethane formulation. The novel photocatalysts provide a technology platform that opens new opportunities for radiation curing in a variety of applications.

Introduction

Over the past decades, radiation curing has found an increasing number of industrial applications. Major reasons for this development are the unique features of this technology, which allow the realization of considerable economic and ecological advantages. These include the use of ready-to-use, solvent-free high-solid formulations with a long shelf life in combination with cure on demand and high cure speed. Other advantages are low temperature processing and the outstanding quality of the products obtained. Radiation curing is thus attractive for applications such as protective and decorative coatings on wood, metal, plastic, paper or glass. In graphic arts, the fast drying time of UV-curable printing or ink jet inks is highly appreciated. Imagewise exposure of photocurable formulations is the base of manufacturing processes that produce structured articles including printing plates or electronic devices such as photoresists or color filters. The layer-wise build-up of three-dimensional objects in the stereolithographic process is another versatile application of radiation curing used for rapid prototyping.

Radiation curable formulations that undergo a radical polymerization are by far most frequently used. This polymerization process is in fact very well suited for the fast transformation of a liquid formulation into a cured material. The activation energy for the addition of a radical to an acrylic carbon-carbon double bond is very low and allows an efficient polymerization to occur at a high rate even at room temperature. Full polymerization can thus be achieved within seconds. One or two initiating radicals produced by the photoinitiator upon absorption of light convert a large number of monomers into a polymeric network. This amplification of the photochemical event by a thermal chain reaction causes the high energy efficiency of the process, which makes it attractive for industrial applications. Not surprisingly a wide variety of raw materials for radically curing systems is thus commercially available, including resin components [1] based on acrylates, unsaturated polyesters or styrene derivatives, and highly efficient photoinitiators [2,3]. Formulations produced thereof can meet the requirements of a broad range of application conditions.

Nevertheless, radically polymerizble systems have some inherent limitations. Oxygen present in the atmosphere reacts with radicals produced from the photoinitiator or on the growing polymer chain, thereby inhibiting an efficient polymerization especially at the surface and in thin layers. The radical addition reaction occurring during the polymerization process results in a considerable shrinkage of the formulation volume. Since this transformation occurs in a very short time that does not allow for relaxation processes, this may result in adhesion problems or the build-up of stress. The high number of crosslinks formed

result in a cured coating that is physically and chemically very resistant, but often lacks flexibility. These issues can be controlled to some extent by the proper selection of resin components, additives and curing conditions. Nevertheless, formulations curing by alternative crosslinking mechanisms that do not suffer from these restrictions would offer attractive solutions for the end user, too.

Light induced cationic polymerization is also known for a long time and is currently used in several industrial applications, although to a much lesser extent than radically curing formulations. The ring-opening reaction occurring in epoxide polymerization results in less shrinkage, and coatings with high flexibility and good adhesion on metal can be obtained. Further, the cationic polymerization process is not inhibited by oxygen. However, humidity in air can have a significant influence on the curing process, since water may act as a chain transfer agent. Furthermore, the ring-opening reaction requires a considerably higher activation energy, and a thermal post-treatment is often required in order to achieve full cure. Vinyl ethers give faster curing systems but have other disadvantages including the relatively high costs of these materials. The choice of cationic photoinitiators is much smaller than that of radical initiators, although several highly efficient compounds are commercially available [4].

The crosslinking of suitable formulations by base-catalyzed reactions is well-known for conventional coatings. A wide variety of crosslinking processes is available for such formulations, including for example the base-catalyzed addition of polyols to polyisocyanate to give polyurethanes [5], the ring-opening of epoxide groups by nucleophiles such as amino, thiol, carboxylate or anhydride groups [6,7], or the crosslinking of acetoacetate or malonate groups containing polyesters with acrylate groups by a base-catalyzed Michael reaction [8,9]. Curing of epoxides by imidazole derivatives is an example of a base-catalyzed homopolymerization [6].

Coatings with outstanding properties can be obtained by these base-catalyzed curing reactions, and several of these systems find widespread use in industrial applications. The catalyst is usually added in a non-latent form, which results in an immediate initiation of the crosslinking process after the addition. These systems can thus only be used as two- component formulations that have to be applied within a short time after mixing. Only very few exploratory studies on the possibility of using photodeblockable catalysts for such resins have been reported so far in the literature. This is mainly due to the lack of suitable photolatent bases.

The availability of such photolatent catalysts, which are blocked and stable in the dark, but liberate an active amine upon irradiation, could greatly broaden the application range of base catalyzed resins. It would allow the development of one-component formulations with a long pot life, or alternatively two-component systems that have an extended working window. Curing would occur "on demand" when the coating is irradiated with a suitable light source. These features would provide similar economic and ecological advantages to this resin chemistry as for conventional UV-curable systems.
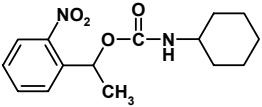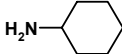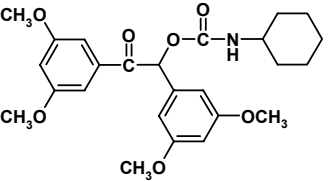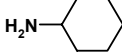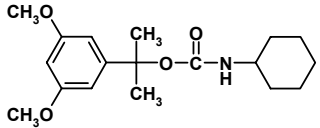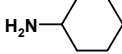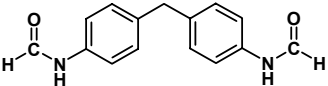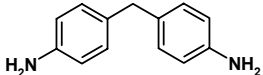
An extension of radiation curing into resin types so far not available for this technology is also interesting in view of the fact that radiat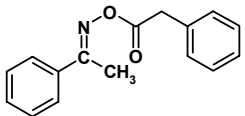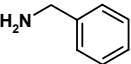ion curing formulations currently make up for only approximately 5% of the whole coating market. The introduction of photolatent base catalyst can open new opportunities and considerably increase the market share for radiation curing. Therefore, we have set out to design suitable photolatent catalysts that can be used for the curing of base-catalyzed formulations.

Photolatent amine catalysts

The photogeneration of amines from blocked precursors has been reported in the literature. Photolabile blocking groups for amines have first been developed and used in organic synthesis as a useful concept for selectively removable protective groups [10]. Primary or secondary amines can thus be generated from non-basic precursors and are subsequently used for further reactions.

These protected compounds have recently also been applied as latent amines for technical applications [11]. In the pioneering work by Fréchet, the possibility of using *ortho*-nitrobenzylcarbamates [12,13] or α,α-dimethyl-benzyloxycarbonyl amines [14] as photolatent amines in resist applications was demonstrated. Benzoin carbamates [12,15], *O*-acyloximes [16], formanilide or acetanilide derivatives [17] and cobalt amine complexes [18] were later added to the toolbox for similar use (Table 1).

Table 1.   Different classes of photolatent amines reported in the literature.

latent amine class	blocked amine	photochemically generated amine	ref.
ortho-nitrobenzyl carbamates			[12]
benzoin carbamates			[12]
α,α-dimethyl-benzyloxycarbonyl amines			[14]
O-acyloximes			[16]
formanilide derivatives			[17]

A common feature of all these structures is that they produce primary or possibly secondary amines upon irradiation. Only a few coating applications of such derivatives have been reported. Photogenerated primary amines can for example act as crosslinkers in reactions with epoxides [18-20] or isocyanates [19]. In this process, one photogenerated amine can form one or at most two crosslinks (Figure 1). It does, however, not act as a catalyst, which could facilitate a multitude of crosslinking reactions without being consumed. During the curing process, the photochemical event is thus not multiplied by a repetitive thermal reaction, and stoichiometric amounts of photons are required with respect to the number of crosslinks to be formed. The lack of a thermal amplification step considerably reduces the

energy efficiency of this concept, which is only applicable for formulations that require a very low number of new crosslinks for complete curing.

Figure 1. **Stoichiometric crosslinking of a polyglycidylacrylate binder by photo-generated ethylenediamine [20]**
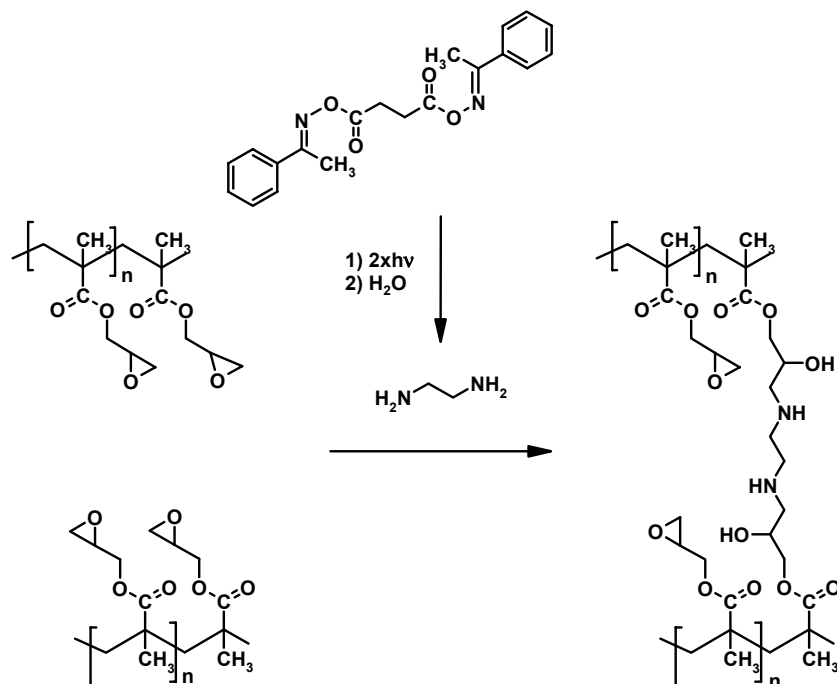
In order to overcome these limits, the photogenerated amine has to act as a real catalyst. Due to their relatively low basicity and high nucleophilicity, primary and secondary amines are usually not very efficient catalysts. Tertiary amines are much more suitable for such use. Only photolatent compounds that can generate tertiary amines are thus potentially useful for the development of an efficiently photocurable formulation.

The type of the tertiary amine produced controls the scope of applications. Simple tertiary amines are sufficiently basic for deprotonation of compounds of high acidity. Thus, simple tertiary amines are capable of catalyzing the crosslinking of epoxides with carboxylates [7]. More elaborated compounds, e.g. 1,4-diazabicyclooctane (DABCO) are also efficient for the catalysis of other crosslinking reactions, such as the reaction of alcohols with isocyanates.

Table 2. **Amines suitable as catalysts for crosslinking reactions (pK$_a$ in aqueous solution [9,21]).**

| trialkylamines	guanidines	amidines	
trimethylamine	1,1,3,3-tetramethyl-guanidine	1,5-diazabicyclo-[4.3.0]non-5-ene	1,8-diazabicyclo-[5.4.0]undec-5-ene
pK$_a$ = 9.8	pK$_a$ = 13.6	pK$_a$ = 12.7	pK$_a$ = 12.5

Amidine-type bases, such as tetramethyl guanidine (TMG), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) or 1,5-diazabicyclo[5.4.0]-undec-5-ene (DBU) are by 3-4 orders of magnitude more basic than tertiary amines. These compounds are therefore capable of acting as catalysts for reactions that require stronger bases. A typical example is the Michael addition of weakly acidic acetoacetate or malonate derivatives to acrylic double bonds, which is efficiently catalyzed by TMG, DBN or DBU, but not by simple tertiary amines [22].

The photogeneration of tertiary amines is considerably more difficult than that of primary or secondary amines. Tertiary amines are fully substituted on the nitrogen atom. Introduction of an additional photolabile substituent thus inevitably results in the formation of an ammonium salt derivative (Figure 2). The few precursors of tertiary amines reported in the literature are in fact organic salts, such as ammonium salts of phenylglyoxylates [23,24], benzhydryl ammonium salts [25], N-benzophenonmethyl-tri-N-alkylammonium borates [26] or quaternary α-ammonium-acetophenone salts with borate [27] or dithiocarbamate anions [28]. Disadvantages of these salts are their limited solubility in many formulations and a relatively low shelf life due to the ease of nucleophilic substitution reactions occurring at the mostly benzylic substituent in the ammonium salt. In addition, some of these derivatives are only accessible by a difficult synthetic process. A photolatent amine with broad utility should therefore preferentially be an easily accessible neutral compound with acceptable solubility even in formulations of low polarity.

Exchange of one of the substituents of a tertiary amine by a photoremovable group gives neutral photolatent compounds such as N,N-dialkyl substituted carbamate derivatives [29,30]. Such compounds, however, produce secondary amines upon irradiation. Thus, neither the addition of a photoremovable group nor the exchange of one substituent by a photolabile group in a tertiary amine is a viable approach for a neutral photolatent precursor of a tertiary amine. A notable exception is TMG which posses a hydrogen-substituted nitrogen atom. This hydrogen atom has been substituted in one example by a photolatent group to give a neutral compound [31].

Figure 2.   Modification of a tertiary amine by a photoremovable group.

ammonium salt   *tertiary amine*   *precursor of a secondary amine*
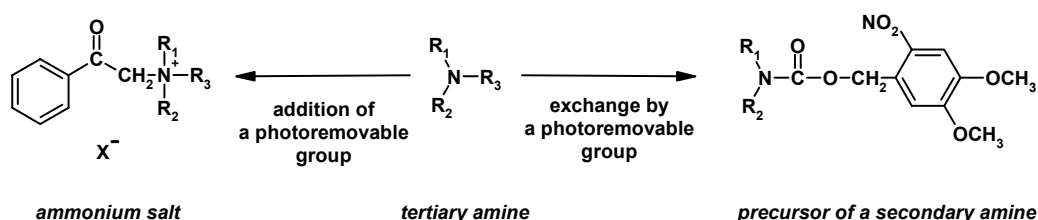
Therefore, two novel concepts for the blocking and photogeneration of tertiary amines were developed in this work. In both approaches the latent and unblocked compounds are tertiary amines. The reactivity of the free amine is, however, considerably increased by the photochemical transformation.

Photoinduced steric release

The electron lone pair in tertiary amines, which have sterically highly crowded substituents around the nitrogen atom, is hardly accessible for nucleophilic reactions. While such sterically shielded amines have a similar basicity for protons as other tertiary amines, they are not efficient as nucleophilic catalysts.

When the steric shielding is reduced by a suitable photoinduced reaction, the catalytic activity of the amine is considerably enhanced. Hence the concept of photoinduced steric

release can be used for the design of photolatent tertiary amines useful as catalysts for crosslinking reactions.

α-Amino substituted acetophenone derivatives are a well-known class of radical photoinitiators that undergo a very efficient α-cleavage reaction [2,3]. These photoinitiators posses a tertiary amino group that is substituted by a highly crowded quaternary carbon atom, carrying *inter alias* a substituted benzoyl group. Calculations suggest a folded configuration for such compounds, in which the nitrogen atom is strongly shielded by the benzoyl moiety (Figure 3) [32]. This folding prevents the nitrogen atom from getting close to a reaction center and forming hydrogen bonds, as it is required in the transition state of base-catalyzed reactions.

Figure 3.   Photoinduced steric release as latency concept for a tertiary amine.

strong steric shielding

initiating radicals for hybrid systems

reduced steric shielding
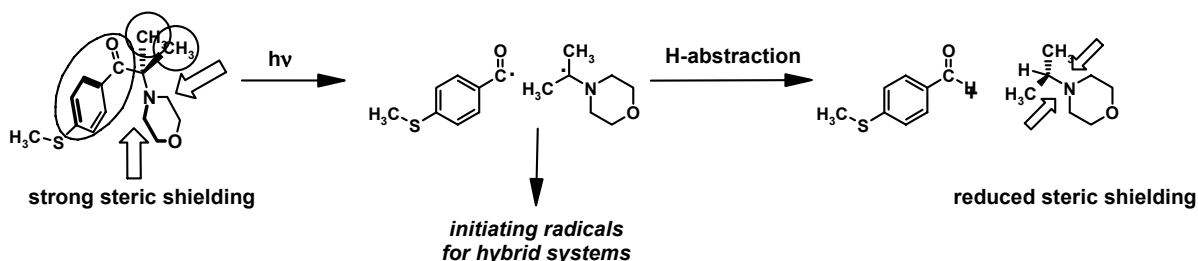
During the photoinitiated cleavage process, the benzoyl group is removed to give an α-aminoalkyl radical [33]. If this intermediate does not react with a double bond, it may produce a new amine *via* hydrogen abstraction. The latter is sterically much less crowded and, according to the calculations, has a stretched conformation that opens the amine for reactions. This compound is hence a more efficient amine catalyst than the photolatent precursor. The photoinduced cleavage of α-amino ketone photoinitiators thus meets the requirements for latency of a tertiary amine based on the photolatent steric release concept.

The efficiency of this approach was demonstrated by the use of these catalysts for the ring-opening addition of carboxylates to epoxides [32]. When followed by differential scanning calorimetry (DSC), the crosslinking reaction in the presence of 1-(4-methylthiophenyl)-2-methyl-2-morpholino-1-propanone starts around 150°C with an exothermic peak temperature above 200°C. Irradiation of the same formulation before the thermal crosslinking results in a reduction of the peak temperature to 150°C with an onset at 70°C. This effect is due to the presence of a more efficient base catalyst after irradiation. Hence photoinduced steric release is a versatile concept for the introduction of latency in tertiary amines.

Since α-amino ketone photoinitiators produce efficient initiating radicals and an active amine in the same photochemical process, they are especially suitable for use in hybrid systems containing both radically and base-catalyzed resin components. These initiators are thus primarily applied in resist materials based on hybrid chemistry [7]. Use in other formulations using only base-catalyzed crosslinkable components is, however, also conceivable.

### *Photoinduced oxidative introduction of an amidine double bond*

The exceptionally high basicity of amidine-type tertiary amines, such as TMG, DBN or DBU, is attributed to the conjugative interaction of two nitrogen atoms *via* the carbon-nitrogen double bond. Elimination of this double bond results in structures with isolated secondary and tertiary amine groups possessing a correspondingly lower basicity. Such compounds

can be used as latent precursors for the much stronger amidine base, if it is possible to introduce the double bond by a photoinitiated oxidation reaction.

Compounds with this property are obtained, when the reduced form of amidine derivatives such as DBN or DBU is alkylated with substituted allyl [34] or benzyl groups [35]. Upon irradiation, these substituents are cleaved with concomitant formation of an amidine double bond. Although the mechanism of this photoreaction has not yet been comprehensively elucidated, irradiation of these compounds is supposed to result in the cleavage of the allylic or benzylic carbon-nitrogen bond (Figure 4). When the carbon-centered radical abstracts a hydrogen atom from the tertiary carbon atom activated by the two amino substituents, the amidine conjugation is introduced. This hypothesis is supported by results obtained with derivatives deuterated in the 6-position of the 1.5-diazabicyclo[4.3.0]nonane moiety, where scrambling of deuterium in the alkyl cleavage product was found.

Figure 4. Photorelease of DBN from an *N*-benzylated precursor.
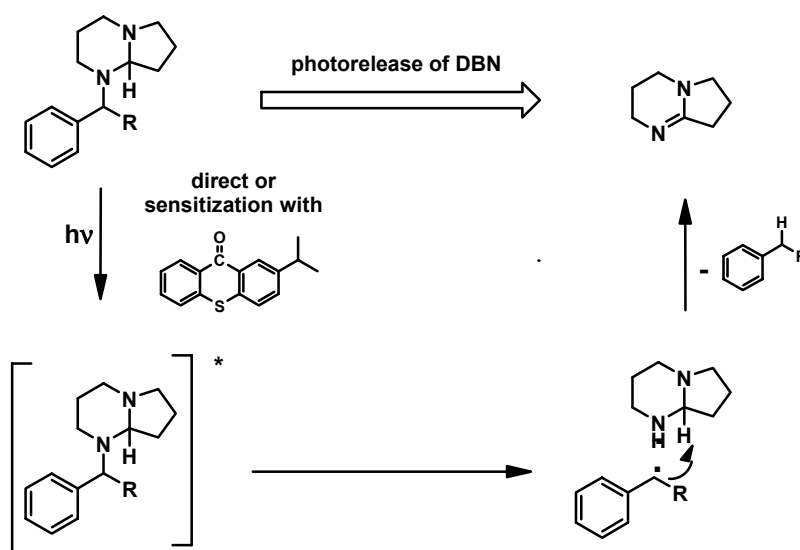
If the assumed reaction mechanism is correct, photodeblocking occurs via a radical reaction. In contrast to the α-amino ketone derivatives discussed before, the intermediate radicals formed in this reaction are not efficient initiating species for radical reactions. In fact they are either highly stabilized allyl or benzyl-type radicals, or α-aminoalkyl radicals located at an unfavorable bridgehead position. Stabilization via hydrogen transfer can thus efficiently compete even in the presence of polymerizable double bonds such as acrylates. These initiators are therefore not suitable for the curing of hybrid-type resins. However, they can be used in formulations containing acrylate oligomers as Michael acceptor compounds, where the homopolymerization of the latter by radical polymerization has to be avoided.

The absorption spectra of these compounds can be tuned over a wide range by the introduction of different substitution patterns on the allylic or benzylic moieties. In parallel, properties such as solubility or physical appearance can be adopted to the requirements of the target application. In the course of an extensive evaluation, 5-benzyl-1,5-diazabicyclo-[4.3.0]nonane has been identified as the most versatile structure both in view of its application properties and the synthetic access.

While the absorption spectrum of this compound is restricted to the UV, the sensitivity can be extended to longer wavelengths by the addition of suitable sensitizers such substituted benzophenone derivatives or 2-isopropyl-thioxanthone (ITX). This is an outstanding ad-

vantage, since the use of UVA or daylight for curing becomes increasingly important especially for outdoor coatings. An application using this photolatent DBN derivative with ITX as sensitizer and artificial daylight for curing is shown in the following.

Radiation curing of a polyurethane coating

Polyurethane resins (PUR) find widespread use in the coatings industry due to the outstanding properties of these lacquers, such as high mechanical and chemical resistance combined with high flexibility and good adhesion properties. These coatings are cured by the polyaddition reaction between a polyol and a polyisocyanate binder component (Figure 5). Due to the inherent reactivity of these functional groups, the crosslinking reaction occurs already in the absence of a catalyst at room temperature albeit at low speed. As a consequence, these coatings are handled as two-component formulations that are mixed shortly before use.

In order to meet the requirement of a short cure time for an industrial application, a catalyst is usually added to accelerate the curing process. Typical catalysts are either metal complexes that are capable of activating the isocyanate groups, such as dibutyltin dilaurate (DBTL), or suitable amines such as 1,4-diazabicyclo[2.2.2]octane (DABCO) or 1,5-diazabicyclo[3.2.0]non-5-ene, which increase the reactivity of the hydroxyl group [5].

Figure 5.   Curing of a 2K PUR model system with suitable catalysts.
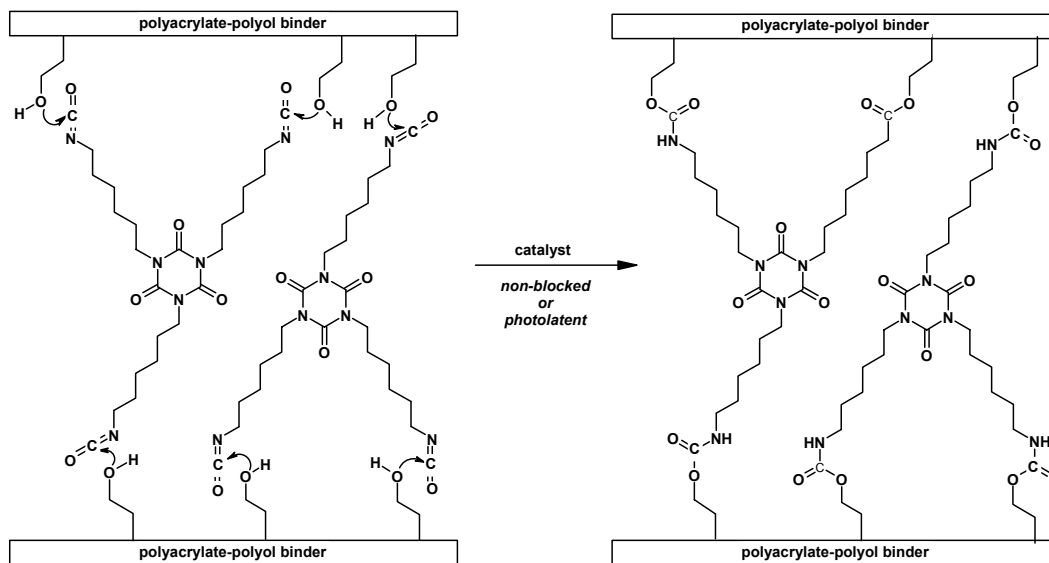
While these catalysts considerably increase the cure speed, they also correspondingly reduce the pot-life of the ready-to-use, mixed two-component system. A useful "application window" is typically defined as time to doubling of the initial viscosity. After that the viscosity of the formulation is too high for most application processes. The development of versatile two-component PUR is thus a compromise between high throughput related to fast cure speed and an acceptable pot-life that minimizes loss of material due to premature gelation. Clearly, a blocked catalyst that allows the extension of the application window without affecting the cure time would be highly desirable for further improvements of such formulations.

Therefore we have evaluated the photolatent DBN-derivative 5-benzyl-1,5-diazabicyclo-[4.3.0]nonane for use in PUR formulations. For these studies, a two-pack polyurethane

model system consisting of a polyacrylate-polyol and a hexamethylene diisocyanate (HDI) type polyisocyanate was selected. This formulation is designed to cure within one day at room temperature in the absence of a catalyst, or within 30 min at 60°C if 0.016% DBTL is added as catalyst.

A comparison of the catalyst efficiency was performed by replacing DBTL with unblocked DBN, the photolatent DBN derivative or a combination of the latter with ITX as sensitizer. Due to the different catalytic activity, DBN was used at a higher concentration than DBTL for similar efficiency. The photolatent derivative was used at an even higher concentration in order to compensate for the approximately doubled molecular weight and the intrinsic photoefficiency of the photolatent DBN: In fact it must be expected that photodeblocking is not complete during the light exposure time and thus only a fraction of the latent catalyst is transformed into active DBN.

After mixing of the two components and the catalyst, the PUR formulations were applied with a slit coater on 30 cm long glass plates. Curing of the samples was monitored using a drying recorder from Byk-Gardner, where a needle is moving during 24 hours with constant speed over the whole length of the coated substrate. Evaluation of the trace in the coating allows an assessment of the curing process, which can be divided into three steps: Phase 1 corresponds to the evaporation of the solvent, phase 2 is a first crosslinking, and on completion of phase 3 a tack-free coating is obtained. As is customary for such coatings, crosslinking reactions will go on for a while until full through-cure is achieved. From an application point of view, however, the achievement of a tack-free surface with no further dust uptake is considered the crucial step. The reactivity evaluation was performed using artificial daylight lamps as radiation source, which simulates constant natural light conditions, for the photorelease of the catalyst.

Figure 6.   Drying time a 2P PUR a) without a catalyst; b) with conventional DBTL; c) with unblocked DBN; d) with photolatent DBN under artificial daylight; e) with photolatent DBN and ITX under artificial daylight.
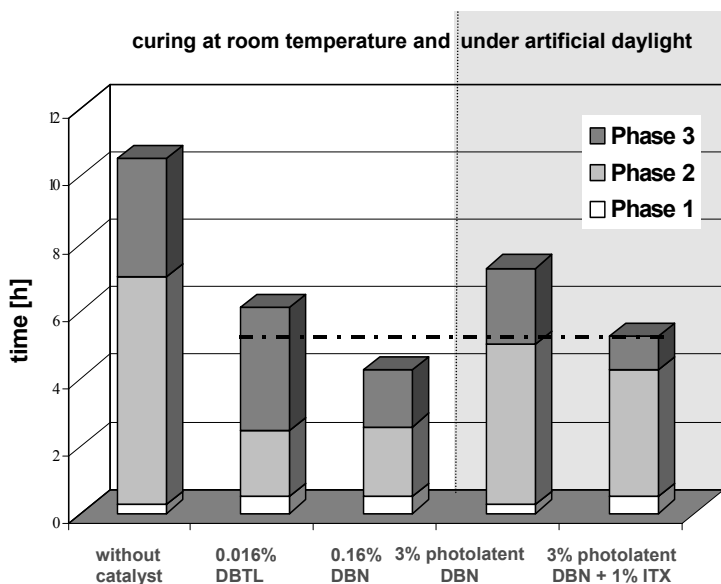

The results displayed in Figure 6 show that a cure time in the same range as that obtained with the state-of-the-art catalyst DBTL can be achieved when the photolatent DBN derivative is used in combination with ITX as sensitizer. Not surprisingly, the curing efficiency is lower when the photolatent compound is used without sensitizer, since the absorbance of

light in the UVA/visible range is considerably higher for ITX than for the photocatalyst. All cure times are measured at ambient temperature and could be further reduced, if an additional thermal treatment would be applied, as it is often the case in applications using DBTL as catalyst. Alternatively, using radiation sources with a higher emission in the UVB can reduce the cure time of the formulations using the photolatent DBN catalysts due to the higher photoefficiency achieved at these wavelengths.

The pot-life of the ready-to-use formulations containing the catalysts was measured in the dark using an ICI cone & plate viscometer. The time-dependent increase of the viscosity of the different formulations is shown in Figure 7. The viscosity of the formulation containing DBTL as catalyst doubles at room temperature within 60 to 90 min, which is conterminous with loss of applicability. In contrast, the formulations containing either the photolatent DBN derivative alone or in combination with ITX show only a slow increase of viscosity, which is in the same range as that of the non-catalyzed formulation. This equals out to an extended pot-life, which allows application of the formulation over a whole working day instead of less than two hours. Only when the applied formulation is exposed to light, fast crosslinking starts, to give the cured coating in the same time frame as with an unblocked catalyst.

Figure 7.   Pot-life of the ready-to-use 2K PUR formulations containing different non-blocked and photolatent catalysts.
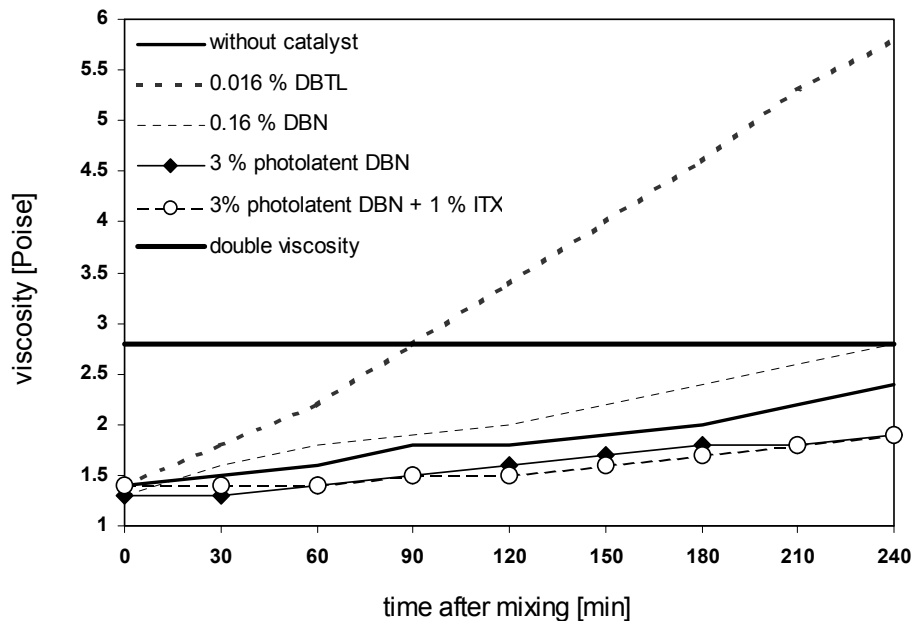
These results are experimental proof for the different catalytic activity of the photolatent DBN derivative and unblocked DBN, as well as for the efficient photoinduced release of the latter from the blocked precursor. They translate into outstanding advantages for industrial applications of 2K PUR lacquers: The extended application window greatly facilitates the handling of the formulation and reduces losses, while no compromise on cure speed compared to the state-of-the-art has to be made due to the "cure on demand" triggered by light. In addition, the slow dark cure of the formulation results in a cured coating even in areas that were not or insufficiently exposed to light, as it may be the case for coatings applied on three-dimensional objects, thereby eliminating one of the limitations in the application of radiation curable coatings.
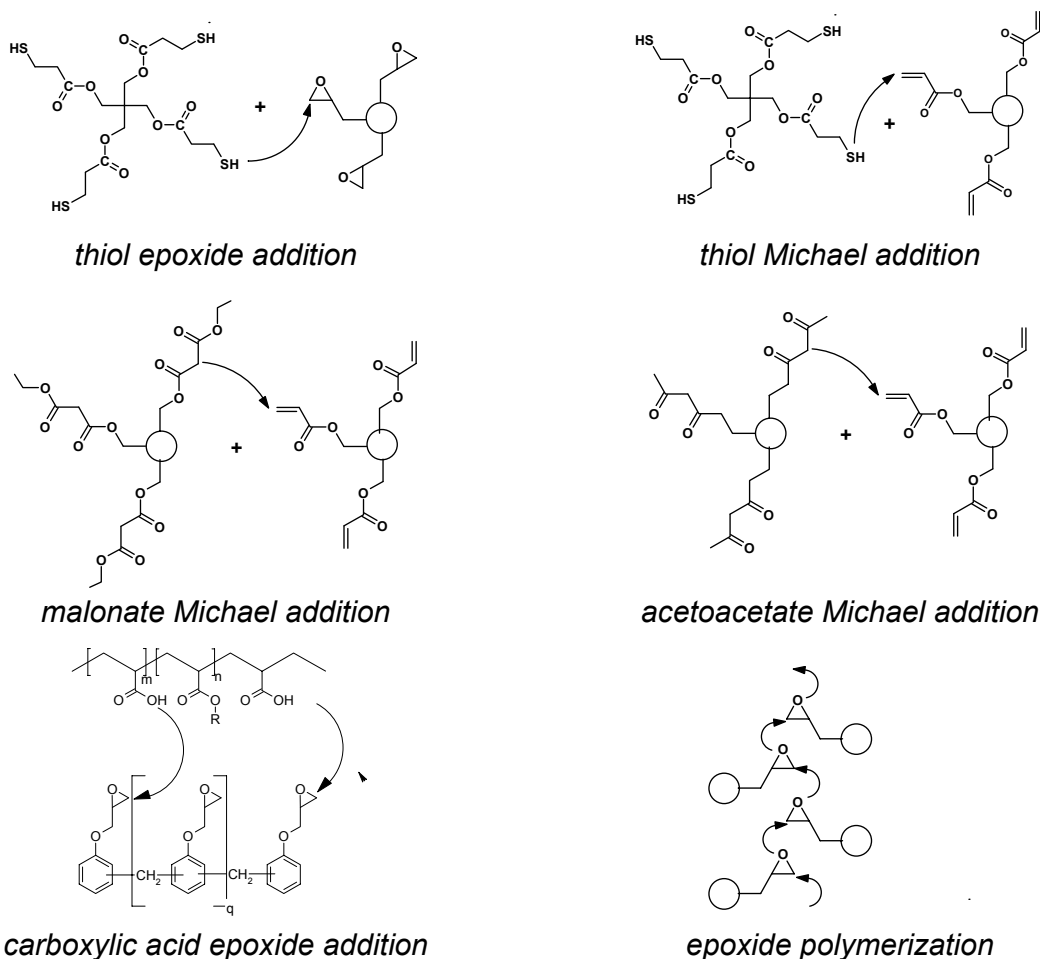
Conclusion

The development of photoinitiators that release tertiary amines and amidine-type catalysts opens new opportunities for radiation curing. The light-triggered curing of formulations that cure by a base-catalyzed mechanism becomes now possible. A wide variety of such resins are known in the literature (Figure 8). Depending on the crosslinking mechanism and the application conditions, the careful selection of a photolatent base producing an appropriate catalyst is an important precondition for efficient curing. The use of sensitizers has proven to be a useful tool for the optimization of the light sensitivity to the irradiation conditions.

Depending on the resin 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. The improved handling conditions due to an extended pot-life in combination with fast curing upon irradiation provide considerable advantages for the end user. 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. Examples are formulations which crosslink via the Michael addition of weakly acidic β-ketoesters or malonates to suitable acceptors.

The accessibility of radiation curing for base-catalyzed formulations thus provides a new technology platform that allows the use of both established or newly developed resin types under new and attractive curing conditions.

Figure 8.   Different crosslinking mechanisms catalyzed by the photolatent base technology.

thiol epoxide addition

thiol Michael addition

malonate Michael addition

acetoacetate Michael addition

carboxylic acid epoxide addition

epoxide polymerization

References

[1]   N. S. Allen, M. A. Johnson, P. K. T. Oldring, M. S. Salim, *Prepolymers and reactive Diluents for UV and EB Curable Formulations,* Vol. 2 in the series *Chemistry & Technology of UV and EB Formulation for Coatings, Inks & Paints* (P. K. T. Oldring, ed*.),* SITA Technology, London 1991

[2]   K. Dietliker, J. V. Crivello in *Photoinitiators for Free Radical Cationic & Anionic Photopolymerization, 2nd Edition* Vol. 3 in the series *Chemistry & Technology of UV and EB Formulation for Coatings, Inks & Paints (*G. Bradley*, ed.),* John Wiley and Sons/SITA Technology, London 1998, chapter II.

[3]   K. Dietliker, *A Compilation of Photoinitiators Commercially Available for UV today* SITA Technology Limited, Edinburgh/London 2002.

[4]   J.-L. Birbaum, S. Ilg, *RadTech Europe 2001,* Basel, Conference Proceedings, p. 545, 2001.

[5]   D. Stoye, W. Freitag, Lackharze, Hanser (Munich) 1996, p. 186.

[6]   J. M. Barton, Adv. Polym. Sci. **1985**, *72*, 11.

[7]   J.-L. Birbaum, M. Kunz, A. Kimura, H. Kura, H. Oka, H. Nakashima*, Eur. Pat. Appl. 898202 A1* (1999).

[8]   A. Noomen, Prog. Org. Coatings **1997**, *32*, 137.

[9]   W. Erdle, K.-H. Vogel, R. Tinsley Farbe+*Lack* **2004**, *2*, 22.

[10]   R. W. Blinkley, T. W. Fletchner in *Synthetic Organic Photochemistry* (W. M. Horspool, ed.), Plenum Press, New York 1984, p. 407.

[11]   K. Dietliker, J. V. Crivello in *Photoinitiators for Free Radical Cationic & Anionic Photopolymerization, 2nd Edition* Vol. 3 in the series *Chemistry & Technology of UV and EB Formulation for Coatings, Inks & Paints (*G. Bradley*, ed.),* John Wiley and Sons/SITA Technology, London 1998, chapter IV.

[12]   J. F. Cameron, J. M. J. Fréchet, *J. Am. Chem. Soc* **1991**, *113*, 4303.

[13]   J. F. Cameron, C. G. Willson, J.M.J. Fréchet, *J. Am Chem. Soc.* **1996**, *118*, 12925.

[14]   J. F. Cameron, J.M.J. Fréchet, *J. Org. Chem*. **1990**, *55*, 5919.

[15]   J. F. Cameron, C. G. Willson, J. M.J. Fréchet, *J. Chem. Soc., Perkin Trans. I* **1997**, 2429.

[16]   K. Ito, M. Nishimura, M. Sashio M. Tsunooka, *J. Polym. Sci. Part A: Polym. Chem*. **1994**, *32*, 2177.

[17]   T. Nishikubo, E. Takehara, A. Kameyama, *Polym. J*. **1993**, *25*, 421.

[18]   C. Kutal, G. Willson, *J. Electrochem. Soc*. **1987**, *134*, 2280.

[19]   T. Nishikubo, E. Takehara, A. Kameyama, *J. Polym. Sci. Part A: Polym Chem*. **1993**, *31*, 3013.

[20]   K. Ito, M. Nishimura, M. Sashio, M. Tsunooka, *J. Polym. Sci. Part A: Polym Chem*. **1994**, *32*, 1793.

[21]   *Handbook of Chemistry and Physics*, 62nd edition, p. D-141.

[22]   R. J. Clemens, F. Del Rector, *J. Coat. Technol*. **1989**, *61*, 83.

[23]   W. Mayer, H. Rudolph, E. de Cleur, Angew. Makromol. Chem. 1981, 93, 83.

[24] A. Noomen. H. Klinkenberg, *Eur. Pat. Appl. 448154 A1* (1990).

[25] J. E. Hanson, K. H. Jensen, N. Gargiulo, D. Motta, D. A. Pingor, A. E. Novembre, D. A. Mixon, J. M. Kometani, C. Knurek, *Polym. Mater. Sci. Eng*. **1995**, *72*, 201.

[26] A. M. Sarker, A. Lungu, D. C. Neckers, *Macromolecules* **1996**, *29*, 8047.

[27] G. Baudin, S. C. Turner, A. F. Cunningham, *PCT Pat. Appl. WO 0010964* (2000).

[28] H. Tachi, T. Yamamoto, M. Shirai, M. Tsunooka, *J. Polym. Sci. Part A: Polym. Chem*. **2001**, *39*, 1329.

[29] M. R. Winkle, K. A. Graziano, *J. Photopolym. Sci. Technol*. **1990**, *3*, 419.

[30] A. Mochizuki, T. Teranishi, M. Ueda, *Macromolecules* **1995**, *28*, 365.

[31] W. A. D. Stanssens, J. F. G. A. Jansen, *PCT Pat. Appl*. WO 9731033 (1996).

[32] H. Kura. H. Oka, J.-L. Birbaum, T. Kikuchi, *J. Photopolym. Sci. Technol*. **2000**, *13*, 145.

[33] G. Rist, A. Borer, K. Dietliker, V. Desobry, J.-P. Fouassier, D. Ruhlmann *Macromolecules* **1992**, *25*, 4182.

[34] S. C. Turner, G. Baudin, *PCT Pat. Appl*. WO 9841524 (1998).

[35] G. Baudin, K. Dietliker, T. Jung, *PCT Pat. Appl*. WO 0333500 (2003).