



Photolent amines producing a strong base as photocatalyst for the *in-situ* preparation of organic–inorganic hybrid coatings



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ABSTRACT

A photolent amine producing the strong nitrogen base DBN was shown to be an efficient catalyst for triggering the concomitant base-catalyzed crosslinking of an organic thiol/epoxide formulation and the formation of inorganic nanoparticles from suitable precursors. Organic–inorganic hybrid coatings containing well-dispersed inorganic silica or zinc oxide nanoparticles were thus obtained and analyzed. The combination of the properties of these nanoparticles with the features of the organic matrix provides coatings with outstanding characteristics.

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1. Introduction

Radiation curing is well established as an environmentally friendly technology providing numerous technical and economic benefits to the user [1–5]. While some of the current applications are already mature technologies, the attractive features of this process continue to stimulate further developments into application fields providing added values beyond simple curing.

Currently most applications are based on photoinitiated radical polymerization, mainly because of the commercial availability of a large variety of radical photoinitiators, reactive monomers and oligomers, which allows the design of formulations meeting most requirements of industrial applications [6,7]. Although used to a lesser extent, photoinduced cationic polymerization is another established radiation curing technology which provides properties different from radically curing systems and is thus a versatile alternative for applications where the photoinduced radical polymerization does not give satisfactory results [7,8].

In contrast to the photoinduced radical or cationic polymerization, phototriggered base-catalyzed crosslinking reactions have for a long time attracted little interest in radiation curing. One reason for the slow acceptance of this technology was the lack of suitable

photolent base catalysts. Although the use of photogenerated amines as coupling agents in photographic process was reported as early as 1972 [9] and first applications for the curing of organic resins date from 1981 [10], the development of suitable photolent base catalysts started only in the 90s [11]. The first examples of photolent amines used in radiation curing produced primary or secondary amines which are useful as crosslinkers but cannot be used as catalysts. Thus only few applications were reported for coatings or adhesive materials until a short time ago [12,13].

The recent development of photolent tertiary amines that produce a base capable to act as true catalysts for crosslinking reactions was a remarkable break through opening new opportunities to develop photobase-catalyzed formulations that can be cured with high efficiency. The successful introduction of a commercial application using a photolent base producing a tertiary amine as trigger for the curing of a car refinishing coating is a first proof for the practical viability of the photobase technology also for coatings and adhesive applications [14].

Besides organic resins, inorganic networks are of high interest for many applications in view of their outstanding properties that are not matched by organic materials. Typical examples are siloxane networks that can be obtained from low-molecular precursors by sol-gel reactions involving acid- or base-catalyzed hydrolysis and condensation steps [15]. In view of the obvious advantages provided by light controlled processes, phototriggered sol-gel processes have found much interest over the last years. Due

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to the commercial availability of suitable photolabile acids it is not surprising that most work in this field has been performed using acidic sol-gel reaction conditions [16]. More interesting than the formation of exclusively inorganic materials and thus more extensively investigated is the preparation of organic/inorganic hybrid materials which combine the properties of an organic polymer network with those of an inorganic material in the form of an interpenetrating network or inorganic nanoparticles embedded in the organic matrix. While the sol-gel reactions are always catalyzed by the photogenerated acid, the organic network can be obtained by a reaction catalyzed by the same acid [17–20], or alternatively via a dual cure process involving a second polymerization reaction such as for example photoinduced radical polymerization [18, 20, 21].

Much less work than on photoacid-catalyzed sol-gel processes has been performed on photobase-catalyzed sol-gel reactions although such reactions are of high technical interest. The base-catalyzed process involves a different hydrolysis/condensation mechanism than the acid-catalyzed reaction, resulting in materials with different properties, such as, e.g. silicate film morphology, texture or optical properties. Moreover the use of strong acids is not appropriate for all applications. First applications using inorganic cobalt(III)amine complexes as photobase for a sol-gel reaction have been reported for micropatterning of thin films [22]. However, since the absorption of these latent catalysts is limited to wave lengths in the UV-C range and only a relatively weak amine base is generated, long irradiation times and a postbaking at 400 °C are required which is not feasible for many applications. Recently, the use of organic α -amino ketone photoinitiators as photolabile amines [23] has been shown to provide a tool that allows realizing the sol-gel polymerization of methoxysiloxane precursors without the need for solvent and water or an additional thermal step despite the relatively low basicity of the generated base [24]. As for the acid-catalyzed process, organic/inorganic hybrid systems are most interesting in view of combining properties of an organic coating with those of inorganic materials.

In fact, the use of a photolabile base allows combining the sol-gel process with organic resins that can be crosslinked by a base-catalyzed reaction, thus opening the possibility to develop new organic/inorganic hybrid materials not available by cationic or radical polymerization. First applications of simultaneous sol-gel and anionic photopolymerization have recently been reported [25]. *O*-Acylloxime derivatives [26] or α -amino ketones were investigated as photolabile amines, producing either primary or tertiary alkylamines. In combination with 3-(glycidylpropyl)trimethoxysilane as hybrid monomer, the primary amines did not result in sufficient crosslinking, while the tertiary amine resulted in the crosslinking of both the siloxane and epoxy moieties. However, since the basicity of the amine catalyst is rather low, a thermal postbaking was necessary in order to obtain a fully cured film. In comparison with a photoacid-initiated system, it was shown that full conversion of the silanol condensation reaction took considerably longer than the acid-catalyzed reaction. This can in part be explained by the different reaction mechanisms, but was also attributed to the low nucleophilicity of the tertiary amine catalyst [27]. Thus it is highly desirable to use photolabile amine catalysts that can release amines of higher catalytic efficiency than simple tertiary amines.

DBN (1,5-diazabicyclo[4.3.0]non-5-ene) and DBU (1,5-diazabicyclo[5.4.0]undec-5-ene) are among the most powerful organic nitrogen bases [28]. In fact, these amidine bases combine a basicity which is by 3–4 orders of magnitude higher than that of conventional tertiary amines with a high nucleophilicity. As a consequence both DBN and DBU are well-known catalysts for many transformations including crosslinking reactions used for coatings

[29,30]. Therefore efforts to develop photolabile precursors of these bases were made since the early days of photolabile base technology. In fact, a first example of a photolabile DBN derivative was reported in 1996 [31], following an early concept of blocking amines in the form of photolabile phenylglyoxylate salts [10]. The same concept was recently renewed [32] and modified using ketoprofen or xanthene acetic acids as photolabile protective groups [33,34] (Fig. 1a). While such compounds are easily available and provide an acceptable photoefficiency, the limitation of this approach is the insufficient shelf life of formulations containing such photolabile amines, which are in equilibrium with the corresponding free amine acting as a non-blocked catalyst.

More useful photolabile DBN and DBU derivatives were obtained in the form of amidinium borate salts [35,36] (Fig. 1b). While the shelf life stability of formulations containing such *N*-(2-aryl-2-oxo-ethyl) ammonium salts is improved as compared to simple carboxylate salts, the use of these photolabile bases is limited by the low compatibility of the ionic derivatives with many formulations.

A further step toward industrially useful photolabile DBN and DBU derivatives was achieved with the introduction of benzylated 1,5-diaza[4.3.0]nonane (Fig. 1c) or 1,5-diaza[5.4.0]undecane derivatives [37,38]. As neutral organic compounds, these derivatives are stable and easily incorporated into resin formulations. Only after irradiation the active base catalyst is liberated, presumably via a homolytic cleavage of the benzylic carbon–nitrogen bond, followed by hydrogen transfer resulting in the formation of the amidine double bond responsible for the strong basicity of amidine bases. It should be noted that the latent form (Fig. 1c) is also a tertiary amine, however of much lower basicity and thus not capable to efficiently catalyze crosslinking reactions.

Thus these benzylated derivatives meet the requirements for industrially useful photolabile catalysts. In the meantime many industrial applications of these photolabile DBN derivatives have been reported [39–45]. Interesting applications include for example crosslinking via a base-catalyzed Michael addition reaction [46,47] or the addition of thiols to epoxides [48,49]. Recently the same benzylated 1,5-diaza[4.3.0]nonane derivatives have also been used as photolabile DBN precursors catalyzing the addition of thiols to episulfides [50] and isocyanates [51], providing polymers with a high content of thioether and thiourea groups and a correspondingly high refractive index which is useful for optical applications. Further applications have been developed based on the crosslinking of siloxane-terminated organopolymers [52–54].

It was therefore of high interest to investigate the efficiency of these photolabile amines producing a strong nitrogen base as photocatalysts for triggering the concomitant base-catalyzed crosslinking of an organic and an inorganic part in novel hybrid systems.

2. Experimental

2.1. Materials

Trimethylolpropane-3-mercaptopropionate (**TH**) was obtained from Bruno Bock Chemische Fabrik GmbH. 3,4-Epoxy cyclohexylmethyl-3,4-epoxycyclohexanecarboxylate epoxy resin (**CE**), tetraethoxysilane (**TEOS**), 3-mercaptopropyl-trimethoxysilane (**MPTS**) and zinc acetate were provided by Aldrich. The photolabile base (**PLB**) (4-(hexahydro-pyrrolo[1,2-*a*]pyrimidin-1-ylmethyl)-benzoic acid methyl ester) [38] was a gift from BASF Schweiz AG. All materials were used as received. The chemical structures of the monomers and photoinitiator are reported in Fig. 2.

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