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# Study on synthesis and photoactivity of N-substituted diazabicyclononane derivatives with different substituents

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## ABSTRACT

N-substituted diazabicyclononanes with different benzylic substituents were synthesized by hydrogenating diazabicyclononene with  $\text{LiAlH}_4$  and alkylating secondary amine with halobenzyl derivatives. The synthesized diazabicyclononanes were identified with NMR spectrometry; the UV absorption and fluorescence emission of the diazabicyclononanes were examined with spectroscopes; the reactivity of the diazabicyclononane as radical photoinitiator and photolatent base were evaluated with DSC, FTIR spectroscopy and gel fraction determination; the effects of substituents on the photoactivities of the diazabicyclononanes were investigated. Electron conjugation in the substituents played a prominent role on the photoactivity. As the conjugation extended, the extinction coefficient increased and fluorescence decreased; meanwhile, the UV absorption expanded towards low frequency. For diazabicyclononane N-substituted with 4-methylene benzophenone, the maximum absorption appeared around 256 nm with extinction coefficient  $1.78 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$ . It could work as radical photoinitiator and photolatent base simultaneously. With this diazabicyclononane, epoxy acrylate could be UV cured within seconds and the activation temperature of epoxy/anhydride could be reduced  $50^\circ\text{C}$  after UV excitation. The gel fraction of acrylate/epoxy hybrid resins could be about 90% after UV-thermal dual curing.

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## 1. Introduction

Currently, photoinitiators used in UV curable resin compounds are either radical or cationic [1–3]. Under UV radiation, the radical photoinitiators release free radicals that can initiate the polymerization of unsaturated acrylic oligomers; whereas the cationic photoinitiators give off acidic species that can catalyze the cationic polymerization of epoxy resins and vinyl ethers. Because radical polymerization proceeds at extreme high rate, radical UV curing may be realized within a second. But if the oligomers are compounded with additives that obstruct UV transmission, such as fillers and pigments, the photoinitiators in the bottom layer are hard to release free radicals and the oligomers will not be fully cross-linked. Cationic UV curing is not so sensitive to shadowing as the radical one because cationic species have long lifetime. Active cations may migrate and grow continually after UV exposure. But the reaction rate of cationic polymerization is low. Cationic UV curing may need minutes of UV exposure [1,4]. Also, acidic species from cationic photoinitiators may corrode substrates [5]. Filled resin compounds are UV cured scarcely.

For advanced adhesives with functional fillers, such as anisotropic conductive adhesives for chip on glass (COG) packaging and phosphor adhesives for light emitting diode (LED) chip potting [2,6], thermal curing has to be used. It not only consumes more energy but also results in thermal stress, narrows material's selection and reduces productivity. To overcome the drawbacks of conventional UV curing technology and enlarge the applications of UV curing, many efforts have been devoted to novel UV curing techniques. Dual curing is one of the exploiting techniques, by which oligomers are cross-linked in two sequential reactions [7,8]. One proceeds during UV irradiation and the other is promoted after UV irradiation. Photolatent base, which releases basic species under UV irradiation [9], is an important topic in this research area. Actually, photolatent base is an extension of photolatent acid, i.e. the cationic photoinitiator [10]. But photolatent bases have few corrosion problems. Indeed, a good many base-catalyzed anionic polymerizations have been utilized in adhesives and coatings [11], such as the addition of isocyanate with polyol and thiol, epoxy with anhydride and thiol, acrylate or acetoacetate with thiol and so on. But these oligomer systems have rarely been used in UV curable formulations because photolatent bases are relatively scarce.

Kutal and his colleagues investigated photolatent bases in 1987 [12]. They irradiated Co(III)-amine salts with UV radiation to

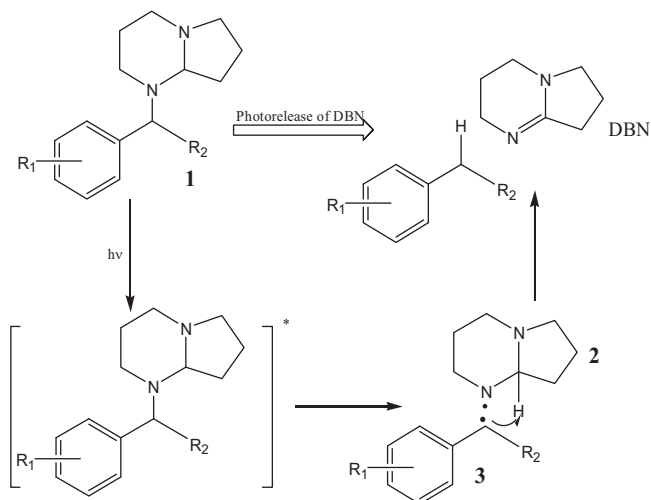
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release ammonia and cross-link oligomers with pendant epoxy. Later, more photolabile bases were developed, including O-acyloximes [13], o-nitrobenzyl carbonyl derivatives [14], carbamates [15], ammonium salts [16,17], and amineimides [18,19], as well as polymers with pendant photolabile bases [20–22]. Most of them released primary or secondary amines under UV radiation and were used for cross-linkers of photoresists [5,22]. In the last decade, researchers have paid attention to photolabile tertiary amines because tertiary amines possess stronger basicity and photolabile tertiary amines may get applications as photolabile catalysts in UV curing. After optimizing the constituents of precursors, tertiary amines could be photo-generated from ammonium salts [17,23,24] and amineimides [19]. But the solubility of ammonium salts is low in most oligomers and the stability of amineimides is poor at ambient temperature.

According to stereochemistry,  $\alpha$ -aminoketone was evaluated as photolabile base [25]. Bulky substituents were introduced to  $\alpha$ -aminoketones to shield the nitrogen atom and impede its catalytic ability. Photolysis might eliminate the steric hindrance and release the active center, thus, enhance the basicity and catalytic ability [26]. Dietliker and his coworkers pointed out that the jump in basicity might come from the alteration of electronic conjugation besides stereochemistry [26,27]. Amidines have two conjugated nitrogen atoms via  $sp^2$  carbon and exhibit super strong basicity. As the conjugation is destroyed, the basicity should drop strikingly. They proposed N-substituted diazabicyclononane derivatives as photolabile bases [28]. Benzyl was selected as the substituent and 5-benzyl diazabicyclononane was evaluated [26,27]. As the diazabicyclononane was photo-excited and the benzylic carbon–nitrogen bond split, the resultant benzyl radical 3 extracted hydrogen from amine radical 2 and gave off diazabicyclononene (DBN), a super strong base [9,27], as depicted in Scheme 1.

They have demonstrated that the benzyl diazabicyclononane is an effective photolabile base for polyol/isocyanate, acetoacetate/acrylate, and epoxy/thiol systems [26,27,29]. However, the details on the synthesis of benzyl-substituted diazabicyclononanes cannot be found in publications. Also, the effects of the substituent on the photoactivity of the diazabicyclononane derivatives have not been studied yet. In this work, N-substituted diazabicyclononane derivatives with different benzylic substituents were synthesized and evaluated as radical photoinitiator and photolabile base. The effects of the substituent on the photoactivity of the diazabicyclononane derivatives were investigated.



Scheme 1. Photolysis of N-substituted diazabicyclononane derivatives [26].

## 2. Experimental

### 2.1. Raw materials

1,5-diazabicyclo[4.3.0]non-5-ene (DBN 99% AR grade) produced by Shandong Xinhua Chemicals was used as the precursor of photolabile bases. Lithium aluminum hydride ( $LiAlH_4$  97%), benzyl chloride, 4-methyl benzyl chloride, methyl(4-bromomethyl)-benzoate, 4-methyl-benzophenone and N-bromosuccinimide (NBS) were AR grade and purchased from Aladdin Reagent Co. Tetrahydrofuran (THF AR grade) was purchased from Guangzhou Chemical Reagent Co. It was dried with calcium hydride for 48 h and distilled prior to use. Epoxy acrylate resin was product EA 621A-80 of Taiwan Changxing Chemicals Ltd. and aliphatic epoxy resin was product CY 179 of Huntsman. Methyl hexahydrophthalic anhydride (MHHPA 98% CP grade) was produced by Puyang Huicheng Chemicals Ltd. All other chemicals and solvents used in this work were AR grade and used as received without further purification unless specified.

### 2.2. Instruments and methods

Nuclear Magnetic Resonance (NMR) spectra were recorded with a Bruker Advance Digital 400 MHz NMR Spectrometer at 400 MHz for  $^1H$  NMR and 101 MHz for  $^{13}C$  NMR. Deuterated chloroform ( $CDCl_3$ ) was used as solvent and tetramethylsilane as reference. UV absorption spectra were acquired on a Hitachi U-3010 UV-vis spectrometer. Samples were dissolved in SP grade acetonitrile at  $10^{-4}$  M. Fluorescent emission spectra were acquired on a Hitachi F-4600 fluorescence spectrometer in  $10^{-4}$  M acetonitrile solution. The wavelength at the maximum UV absorption of the sample was set as the incident radiation. Melting points were measured on a Xinsuo WRS-2 instrument. IR spectra were acquired on a Bruker Vector-22 Fourier Transform Infrared spectrometer. Samples were ground with KBr and pressed into disks. The absorption of  $C=C$  bonds around  $810\text{ cm}^{-1}$  was measured as the relative content of double bonds with the absorption of carbonyls around  $1730\text{ cm}^{-1}$  as internal reference [8,30].

Photo-initiating rate was evaluated in terms of drying time according to GB 1728-79, i.e. the UV exposure time for liquid resin to become non-sticking. Thermal curing was analyzed on a Netzsch Differential Scanning Calorimeter (DSC) 204 F1. Under 20 ml/min of nitrogen stream, about 20 mg of specimen was heated from 40 to 300 °C at 10 °C/min. Heat flow against temperature was reported. The temperature at which the heat flow diverged from baseline by more than 0.05 mW/mg was taken as the temperature of incipient exotherm. Gel fractions were determined based on mass change after specimens were extracted with acetone on a Soxhlet extractor for 48 h.

UV curing was implemented in Uvitron Rayven equipped with a 400 W Intelliray UVA lamp. Liquid resin was cast in 1.0 mm deep Teflon mold and exposed to 60 mW/cm<sup>2</sup> UV radiation for desired time period. Thermal curing was performed in an oven at 100 °C for desired time period.

### 2.3. Synthesis of diazabicyclononane

500 ml THF and 50 mmol DBN were charged to 1000 ml flask. Under stirring, 50 mmol  $LiAlH_4$  was added carefully. Under dry nitrogen stream, the mixture was heated and refluxed for 2 h, and then cooled to ambient temperature. The mixture was cooled to 10 °C in an ice bath and 30 ml aqueous saturated solution of ammonium chloride was applied. The mixture was dried with anhydrous sodium sulfate, gravity filtered and eliminated solvents by rotary evaporation under reduced pressure. The crude product was purified by column chromatography on silica gel with ethyl

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