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A multifunctionalized macromolecular silicone-naphthalimide visible photoinitiator for free radical polymerization

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ABSTRACT

Multifunctionalization strategy in the photoinitiator design keeps in step with the requirement of the green chemistry in photopolymerization techniques. Therefore, a multifunctional macromolecular silicone-naphthalimide visible photoinitiator (SND) has been designed and prepared by a convenient thermal polymerization process of 4-(1,3-dioxo-6-(piperidin-1-yl)-1H-benzo[de]isoquinolin-2(3H)-yl)phenyl acrylate (ND-PA) and 3-bis (trimethylsilyoxy)methylsiyl-propylmethacrylate (TSMSPM). Its structure has been confirmed by ^{1}H NMR, ^{13}C NMR, FT-IR and GPC analysis. On one hand, SND has been evidenced as a visible photoinitiator by its successfully initiating the free radical polymerization of acrylate monomers in the presence or absence of a hydrogen donor under the irradiation of different LEDs (405 nm, 455 nm and 470 nm). Furthermore, SND/MDEA (N-methyldiethanolamine) system shows higher photoinitiating activity than that of the commercial CQ (camphorquinone)/MDEA system. On the other hand, this multifunctionalization strategy also brings about some desired modification for cured-materials. After employing only 5 wt% SND as the photoinitiator, for example, a photo-cured film of urethane diacrylate prepolymer (PUA) increases its water contact angles from 70.1° to 101.2°, implying that SND could change the surface property of the PUA cured film from hydrophilic to hydrophobic. Meanwhile, the use of SND as an initiator could significantly improve the resistance against water and ethanol. When the mass fraction of SND increases to 15%, the water and ethanol absorption ratios of the cured PUA films decrease from 4.4% to 1.0% and 8.9% to 2.8%, respectively.

1. Introduction

Photopolymerization technology that allows the transformation of a liquid monomer into a solid material has obtained widespread applications in traditional and high-tech areas such as coating, adhesives, inks, dental fillings, optical waveguides, micro-electronics and 3D print [1–3]. In general, a photoinitiator acts as a generator of free radicals by the direct fragmentation (Type I), hydrogen abstraction or electron transfer (Type II) upon irradiation and then the radicals initiate polymerization or crosslinking of mono- or multi-functional monomers and oligomers [4–6]. Unfortunately, the conventional low-molecular-weight photoinitiator exists some inherent disadvantages, such as odor, yellowing, migration and poor compatibility with the UV-curable resin, which will lead to undesirable effects in the post-cured materials. Therefore, the development of low odor, nontoxicity, non-yellowing and low migration, one-component macromolecular photoinitiators [7–12] or polymerizable photoinitiators [13–18] have been obtained much more attention. However, these photoinitiators usually will change to the useless components when the photopolymerization completed (Scheme 1A). This is contrary to the requirements of green chemistry, which emphasizes that as many atoms as possible should play roles in the materials. In order to realize the green chemistry requirements of photopolymerization techniques, it may be a good choice to consider integrating the photoinitiating ability and some other additional functions to form a multifunctionalized photoinitiators (Scheme 1B). If it is possible to realize, the multifunctionalized photoinitiator should have undertaken some other roles in the materials when the photopolymerization finished. Thus, the construction of multifunctionalized photoinitiators is of importance in the future development. Despite some photoinitiators with the ability to change the surface properties of the cured films have been reported [19–22], it is still a challenging but attractive task to develop efficient, low odor, nontoxicity, non-yellowing and multifunctionalized photoinitiators for the photopolymerization.

It is well known that urethane-acrylates resins for UV-curable coatings have good mechanical and chemical properties among UV curable resins. However, some weaknesses of polyurethane materials such as poor weathering, poor water/ethanol resistance and their

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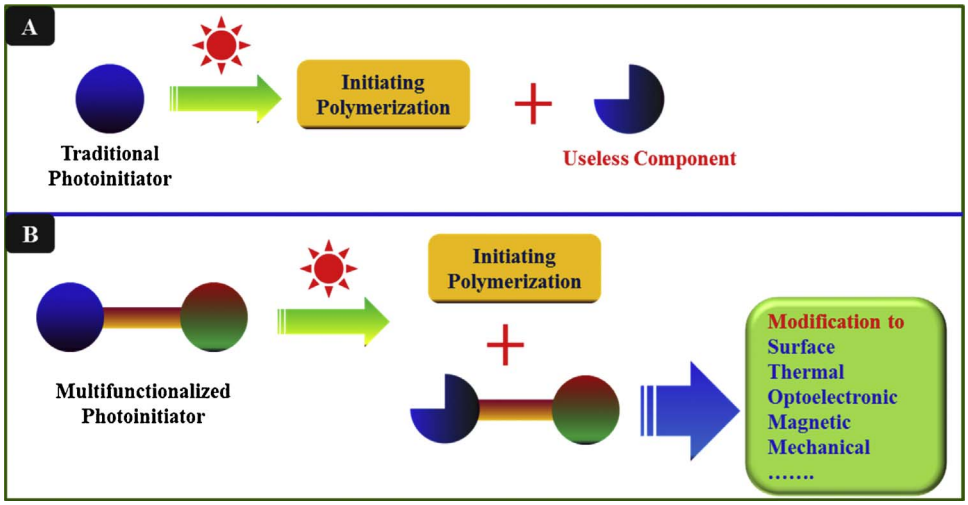


Scheme 1. Schematic illustration of the difference between a traditional photoinitiator and a multi-functionalized photoinitiator.

flammability restrict some of their applications [23,24]. In addition, silicone has been known as an inorganic-organic hybrid polymer material featured with a series of characters such as good chemical and thermal ability, weather-resistance, water-resistance, low friction coefficient, low surface energy and nonstick behavior [25,26]. It is a very useful method to incorporated silicone into the cured films in order to produce high performance UV-cured coatings. [23,27–32] Recently, the search for polymerization upon visible light emitting diodes (LEDs) is the subject of huge interest due to cheap sources, eco-friendly, no ozone release, no harmful UV rays, low operating and maintenance costs and long lifetimes [33]. Some recent reports for specific photoinitiators (PIs) and photoinitiating systems (PISs) suitable for working upon exposure to LEDs can be found [34–39], but the search for high-performance PIs/PISs for visible LED exposure still remains challenges. Among these recently developed versatile visible light sensitive photoinitiators with novel structures, 1,8-naphthalimide derivatives carrying suitable substituents have emerged as the promising candidates for photopolymerization system [40–48]. Although the naphthalimide photoinitators have been obtained outstanding achievements, however, most of these efforts devoted to develop small molecule photoinitators for free radical polymerization, cationic polymerization and free radical promoted cationic polymerization [49,50]. Therefore, a multifunctionalized visible macrophotoinitiator SND (Scheme 2) has been designed and synthesized. Its photopolymerization behaviors and impacts on the properties of the cured films have been investigated. The investigation of its photopolymerization behavior confirms that it's a high efficient visible photoinitiator with the comparable initiating ability to commercial used CQ. Moreover, the incorporation of silicone into the photoinitiator improves the thermal stability of the cured films and dramatically decreased the water and ethanol absorption ratio. Meanwhile, the surface properties of the cured film of polyurethane diacrylate prepolymer (PUA) are changed from hydrophilic to hydrophobic by the addition of SND.

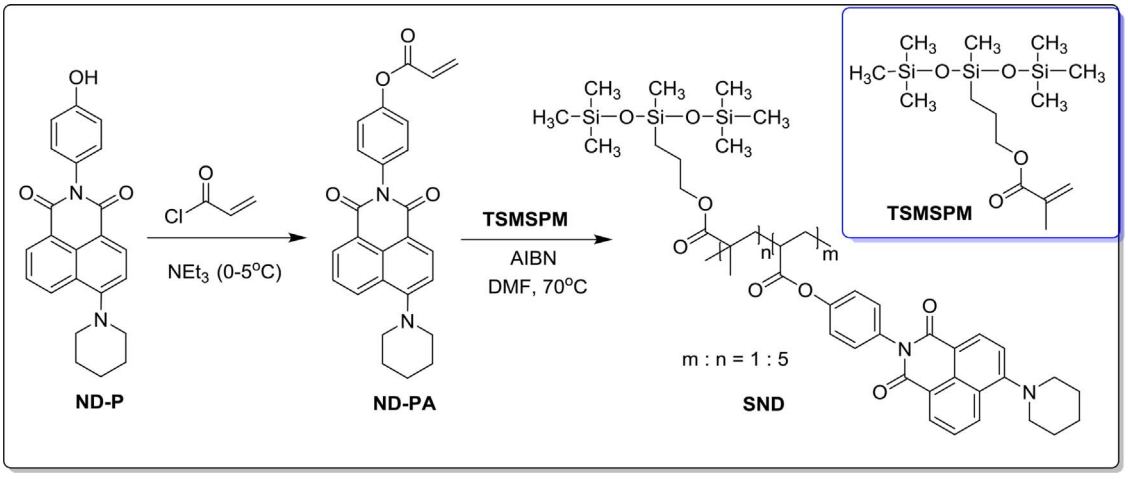
2. Experimental section

2.1. Irradiation sources

Different lights were used for the irradiation of the photocurable formulations: LED centered at 405 nm (~20 mW cm^{-2}), LED centered at 455 nm (~20 mW cm^{-2}), LED centered at 470 nm (~30 mW cm^{-2}). Xenon lamp (HSX-F300, cold light source) with a filter ($\lambda > 400$ nm). The light intensity was determined using a SRC-1000-TC-QZ-N reference monocrystalline silicon cell system (Oriel, USA), which was calibrated by National Renewable Energy Laboratory, A2LA accreditation certificate 2236.01.

2.2. Photopolymerization experiments

For polymerization experiments, the conditions are given in the figure captions, 1,6-hexanediol diacrylate (HDDA), trimethylolpropane triacrylate (TMPTA) were used as active monomers. *N*-



Scheme 2. Synthesis of silicone-naphthalimide macrophotoinitiator SND.