



Naphthalimide dyes: Polymerizable one-component visible light initiators



Jianjing Yang, Wen Liao, Ying Xiong, Qingqing Wu, Xiaoling Wang^{**}, Zhen Li, Hongding Tang^{*}

Engineering Research Center of Organosilicon Compounds & Materials, Ministry of Education, College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, 430072, PR China

ARTICLE INFO

Article history:

Received 30 May 2017
Received in revised form
23 August 2017
Accepted 29 August 2017
Available online 1 September 2017

Keywords:

Naphthalimide
Visible light initiators
Photopolymerization
Migration stability

ABSTRACT

Two of acrylated naphthalimide one-component visible light initiators, 2-((2-(1,3-dioxo-6-(piperidin-1-yl)-1H-benzo[de]isoquinolin-2(3H)-yl)ethyl)(methyl)-amino)ethyl acrylate (ND-N-EA) and ((2-(1,3-dioxo-6-(piperidin-1-yl)-1H-benzo[de]isoquinolin-2(3H)-yl)ethyl)azanediy)bis(ethane-2,1-diyl) diacrylate (ND-N-BEA) have been designed and synthesized. Their structures have been confirmed by HR-MS, ¹H NMR and ¹³C NMR. The photochemical mechanisms are studied by cyclic voltammetry (CV), density functional theory (DFT) calculation, and electron paramagnetic resonance (EPR) spectroscopy. Their photopolymerization behavior and the extractability in the cured films are investigated by real-time FT-IR spectroscopy and UV-visible spectrometer, respectively. Results show that both of them exhibit good photopolymerization initiating performance and high migration stability in their initiated cured films.

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1. Introduction

Over the past few years, visible light free radical photopolymerization has attracted much more academic and technological attention due to its significant advantages in irradiation safety and environmental friendliness in comparison to its UV light counterpart [1–4]. As one of the key components in photopolymerization systems, photoinitiator absorbs light and then generates active radicals to initiate the polymerization [5]. Generally, there are two types of free radical photoinitiators [6]. Type I photoinitiator produces radicals by a direct photofragmentation process (α -cleavage) [7]. Type II photoinitiator undergoes photoexcitation followed by an electron or hydrogen transfer process and then produces the initiating radicals [8–10]. Visible light photoinitiators are almost Type II since the low energy of visible light could not lead to a chemical bond cleavage directly. Thus, they usually take effect accompanying with small molecular hydrogen donors, such as amines, which usually bring about some unpleasant

issues, such as odor, yellowing and migration. Meanwhile, only a small amount of photoinitiator is actually consumed during the polymerization process. The unreacted small molecular photoinitiators and hydrogen donors may migrate to their cured materials surface and eventually go back into the surrounding medium. This disadvantage triggers the development of polymeric [11–13] and polymerizable photoinitiators [14–20]. The polymerizable photoinitiator featured with photosensitizer moiety, polymerizable groups and hydrogen donors in the molecule could not only generate free radicals to initiate photopolymerization, but also could take part in polymerization itself with resin. Therefore, it definitely improves migration stability in the formulation.

Naphthalimide derivatives (NDs) carrying suitable substituents have emerged as promising candidates for visible light photopolymerization [21–24]. Some NDs [25–27] (Chart 1) have been explored and their visible light photoinitiating behavior has been investigated. Among them, **DMAEN1**, **DMAEN2** and **BPND** worked as one-component free radical photoinitiators. In addition, **MANA-1** with a methacrylate in its molecule presented as a polymerizable photoinitiator with excellent photopolymerization performance in free radical polymerization, cationic polymerization and the free radical promoted cationic photopolymerization in the presence of additives (amines, iodonium salt or optionally chlorotriazine). Its migration stability was reasonably improved. But the additives still

^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: 973729680@qq.com (X. Wang), chhdttang@whu.edu.cn (H. Tang).

kept the problems in odor, toxicity, and migration. Thus, it deserves to develop the NDs with hydrogen donors and polymerizable groups incorporated in the same molecule. Following our continuing pursuing for one component visible light initiators [20,28], herein, two of one-component acrylated naphthalimide visible light photoinitiators, 2-((2-(1,3-dioxo-6-(piperidin-1-yl)-1H-benzo[de]isoquinolin-2(3H)-yl)-ethyl)-(methyl)amino)ethyl acrylate (**ND-N-EA**) and ((2-(1,3-dioxo-6-(piperidin-1-yl)-1H-benzo[de]isoquinolin-2(3H)-yl)ethyl)azanediyl)-bis(ethane-2,1-diyl) diacrylate (**ND-N-BEA**) (Scheme 1) have been designed and prepared. Both of them contain a naphthalimide moiety, hydrogen donor and one or two polymerizable double bonds. Their photopolymerization behavior and the extractability in the cured films are investigated by real-time FT-IR spectroscopy and UV-visible spectrometer, respectively.

2. Experimental section

2.1. Computational procedure

DFT calculations were performed on Gaussian 09 program (Revision D09). The ground state (S_0) geometries were optimized with the Becke's three-parameter exchange functional along with the Lee Yang Parr's correlation functional (B3LYP) using 6-31G basis sets.

2.2. Irradiation source

The light source was assembled from xenon lamp (laite optics, XD 300, 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. The irradiation intensity was 50 mW cm^{-2} .

2.3. Polymerization experiments

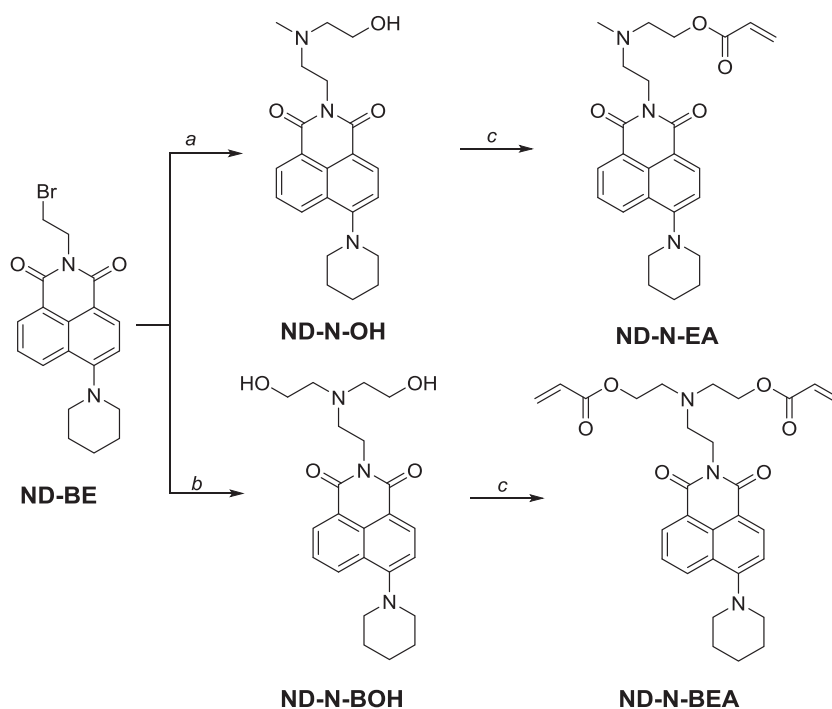
For polymerization experiments, 1,6-hexanediol diacrylate (HDDA), tripropylene glycol diacrylate (TPGDA) and trimethylolpropane triacrylate (TMPTA) were used as active monomers. *N*-Methyldiethanolamine (MDEA) was used as hydrogen donor if needed. The photosensitive formulations consisted of monomers (1.0 g), photoinitiators (PIs: $2 \times 10^{-5} \text{ mol/g}$) and hydrogen donors ($5 \times 10^{-5} \text{ mol/g}$) if needed deposited on a KBr pellet in laminate for irradiation with xenon lamp ($I = 50 \text{ mW cm}^{-2}$). The evolution of the double-bond content was continuously monitored by real-time FT-IR spectroscopy (Nicolet IS 10) at $1610\text{--}1650 \text{ cm}^{-1}$ [29,30]. The degree of double-bond conversion calculated from equation (1) [31,32]:

$$\text{Conversion (\%)} = \left(1 - \frac{A_{X,t}}{A_{X,0}} \cdot \frac{A_{ST,0}}{A_{ST,t}}\right) \times 100 \quad (1)$$

where A_0 and A_t represent the area of the IR absorption peak of functional group of the sample before and after exposure during time t . The subscripts ST and X represent the internal reference ester carbonyl peak at 1730 cm^{-1} and the double bond peak at $1610\text{--}1650 \text{ cm}^{-1}$. The rate-time curvature is obtained by differentiating of conversion-time curvature [30,33]. For each sample, the series RT-IR runs repeated at least three times.

2.4. Redox potentials

The oxidation and reduction potentials of the investigated NDs were measured in acetonitrile by cyclic voltammetry (CV) with tetrabutylammonium hexafluorophosphate (0.1 M) as a supporting electrolyte. The working electrode was a platinum disk and the reference electrode was a saturated calomel electrode (SCE). Ferrocene was used as a standard. The concentration of investigated PIs was $8 \times 10^{-4} \text{ mol/L}$.



Scheme 1. Synthesis of ND-N-EA and ND-N-BEA. a): 2-(methylamino)ethanol, KI, DMF, 110°C , 48 h; b): diethanolamine, KI, DMF, 110°C , 48 h; c): Acryloyl chloride, triethylamine, CH_2Cl_2 , $0\text{--}5^\circ\text{C}$.

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