Available online at www.sciencedirect.com
ScienceDirect
Chinese Chemical Letters 19 (2008) 1071–1074
CHINESE CHEMICAL LETTERS
www.elsevier.com/locate/cclet

Synthesis, characterization and antibacterial properties of multifunctional hindered amine light stabilizers

Yi Deng [a], Wei Chen [b], Tao Yu [b], Li Gong Chen [b,*], Fang Liu [c], Chun Wei Xin [c]

[a] School of Pharmaceuticals & Biotechnology, Tianjin University, Tianjin 300072, China
[b] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
[c] School of chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin 300191, China

Received 8 April 2008

Abstract

A series of novel hindered amine light stabilizers containing an *N*-halamine moiety were designed and synthesized. Their structures were characterized by FT-IR, ^{1}H NMR, and MS. The compounds were tested for antibacterial activity against *Candida albicans*, *Staphylococcus aureus*, and *Escherichia coli*. At a concentration of 0.5 mmol/L, these compounds all exhibited satisfactory antibacterial activity against all the three types of bacteria.

Keywords: Reactive-HALS; Antibacterial property; *N*-Halamine; Synthesis

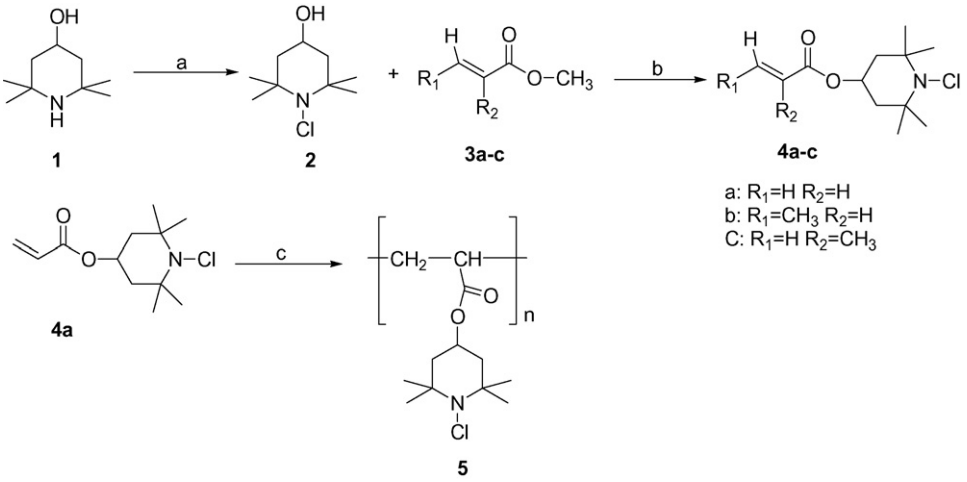
Hindered amine light stabilizers (HALS) are an important class of stabilizers with high photo-stabilization efficiency and excellent compatibility with commercial polymeric materials [1–6]. In the last two decades, the syntheses and investigation of a number of new HALS containing 2,2,6,6-tetramethylpiperidine have been reported [3,4,7–13]. The reactive-HALS monomers and their homopolymers with high molecular weight have been extensively studied because of their excellent applied properties, such as good compatibility, anti-extractability and high solubility [12–15].

In response to the challenges caused by bacteria and microorganisms in medical devices, hospital equipment and food processing devices, antibacterial polymers, which can inhibit the growth of microorganisms, have received both academic and industrial interests [16–20]. To date, these kinds of polymers containing iodine, quaternary ammonium, and phosphonium salts have been widely used [16,19]. Recently, particular attention has been given to *N*-halamine-based polymers which can provide antibacterial function against microorganism without causing environmental concerns [20–24].

In consideration of recent progress in the above two fields, we introduced an *N*-halamine structure to a reactive-HALS molecule resulting in a new type of HALS capable of providing both photo-stabilization and antimicrobial activity. This kind of novel *N*-halamine-based HALS, **4a–c** and **5**, were synthesized via an efficient and simple

* Corresponding author.
E-mail address: lgchen@tju.edu.cn (L.G. Chen).

1001-8417/$ – see front matter
doi:10.1016/j.cclet.2008.06.009



Scheme 1. Synthesis of compounds **4a–c** and **5**. Reagents and conditions: (a) NaClO, 30 °C, 10 h; (b) Ti(O–I–Pr)$_4$, petroleum ether, reflux, 6 h; (c) THF, 60 °C, 24 h.

approach. All the compounds were tested for antibacterial activities against *Candida albicans* (ATCC 10231), *Staphylococcus aureus* (ATCC 6538), and *Escherichia coli* (ATCC 8099).

The synthesis of **4a–c** and **5** was achieved according to Scheme 1. The chlorination reaction of 2,2,6,6-tetramethylpiperidine-1-ol **1** was carried out with a 30 wt% aqueous sodium hypochlorite solution for 10 h and afforded the chlorinate product **2** in 93% yield after recrystallization from petroleum ether [25]. Unlike the method reported by Chen and Sun [22], the buffers were not needed during the reaction and the pH value was not controlled. IR, ^{1}H NMR, MS spectra [25] of compound **2** were in good agreement with its structure.

The transesterification between **2** and **3a** in petroleum ether with tetraisopropyl orthotitanate as a catalyst proceeded effectively to yield **4a** in 82% yield after purification [26,27]. In the ^{1}H NMR spectrum of **4a**, the CH_3 peaks at δ = 1.30 and 1.33 confirmed the presence of the 1-chloro-2,2,6,6-tetramethylpiperidine group and this was further supported by the *O*-CH peaks of 1-chloro 2,2,6,6-tetramethylpiperidine (δ = 5.13–5.17). The peaks for the three double bond protons in **4a** were at δ = 5.82–5.84, 6.09, and 6.38–6.41. The ^{1}H NMR did not detect N–H, which confirmed the formation of the N=Cl bond. The IR spectra of **4a** indicated the presence of a H_2C=CH– double bond (1636 cm^{-1}) and an unsaturated ester bond (1724, 1176 cm^{-1}). The mass spectrum of **4a** contained a molecular ion peak at *m*/*z* 246.0 (M^++1). Compounds **4b–c** were similarly obtained by the transesterification of the corresponding ester **3b–c** [26] and their structures were also verified by MS, IR, ^{1}H NMR spectroscopy [27].

The polymerization of **4a** was carried out in THF at 60 °C for 24 h in the presence of a catalytic amount of 2,2′-azobis(isobutyronitrile) (AIBN), and afforded the polymeric compound **5** in a yield of 70% [28]. In the ^{1}H NMR spectrum of **5**, the double-bond protons peaks of **4a** disappeared after polymerization and the backbone peaks of **5** appeared at about 1.13–2.13. In the IR spectrum of **5**, peaks for the ester bond were observed at 1732 and 1166 cm^{-1}. Upon polymerization, the C=C stretching peak (1636 cm^{-1}) of **4a** disappeared and the aliphatic CH stretching peaks (2755–2976 cm^{-1}) of **5** were more intense than those of **4a**. The gel permeation chromatography (GPC) spectrum of **5** confirmed the formation of high molecular weight polymers. The molecular weight of **5** is M_w = 1150 and M_n = 930. The polydispersity is 1.24.

The bacterial efficacy of **4a–c**, **5** was tested against *Candida albicans* (ATCC 10231), *Staphylococcus aureus* (ATCC 6538), and *Escherichia coli* (ATCC 8099) using hygienic standard for disposable sanitary products method (GB 15979-2002, China). The obtained results are summarized in Table 1.

Compounds **4a–c** were more effective against *Candida albicans* and *Staphylococcus aureus* than against *Escherichia coli*. Compound **4a** showed a 100% inhibitory ratio against *Staphylococcus aureus* at 0.5 mmol/L. Compared with **4a–c**, compound **5** exhibited significantly better activity towards *Escherichia coli* with an inhibitory ratio 96.7%, but it showed only moderate activity against *Candida albicans*.

In summary, novel *N*-halamine-based hindered amine light stabilizers (**4a–c**, **5**) were successfully synthesized via an efficient and simple approach, and their antibacterial activities against *Candida albicans*, *Staphylococcus aureus*, and *Escherichia coli* were studied. Based on this work, the design and synthesis of HALS with more potent