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Synthesis and properties of multifunctional nitroxyl radical hindered-amine light stabilizers

Abstract: A series of novel nitroxyl radical hindered-amine light stabilizer monomers were designed and synthesized from 2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-ol, cyanuric chloride, allylamine, and 2-hydroxyphenylbenzotriazole derivatives. Structures of the new stabilizers were confirmed by ^1H NMR, ^{13}C NMR, FT-IR, ESI-HRMS, and element analysis. The synthesized compounds **5a–f** were evaluated for their antioxidant and antiaging properties, and a significant stabilizing effect against photodegradation was found.

Keywords: 2-Hydroxyphenylbenzotriazole; cyanuric chloride; HALSs; hindered amine; light stabilizers; nitroxyl radical.

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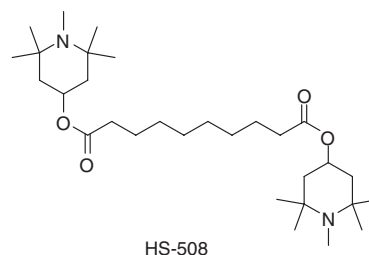
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Introduction

Polymer materials such as polyethylene (PE), polypropylene, polyvinyl chloride, or acrylonitrile butadiene styrene are widely used in our daily life, but they are suffering from the problem of aging. In particular, they undergo degradation when exposed to sunlight, which decreases the use value and shortens their service life, mainly by photo-oxidation [1–3]. Hence, polymeric auxiliaries have been used and studied. Among these additives, attention has been paid to derivatives of 2,2,6,6-tetramethylpiperidine and 2-hydroxyphenylbenzotriazole because of their high photostabilizing efficiency. These two classes of compounds differ in their action, although both are classified as photodegradation stabilizers [4–6]. Hindered-amine light stabilizers (HALSs) are widely used because of their low toxicity, low cost, and excellent compatibilities with a broad range of commercially significant polymeric

materials [7, 8]. HALSs inhibit autoxidation by the transformation of the parent amines to nitroxyl radicals either by reaction with peroxy radicals or occasionally by reaction with singlet oxygen. Oxidative degradation is stopped by the coupling reaction of the nitroxyl radicals with alkyl radicals [9, 10]. In contrast to 2,2,6,6-tetramethylpiperidines, 2-hydroxyphenylbenzotriazoles are assumed to dissipate the absorbed energy in a photophysical manner by converting the absorbed photon energy into heat without being chemically affected [11].

In our previous paper, the combinations of 2,2,6,6-tetramethylpiperidine-4-ol and 2-hydroxyphenylbenzotriazoles derivatives and polymerizable allyl fragments have been described [12]. However, the application of HALSs is constrained because of their relatively high basicity. In the process of polymer production, HALSs readily react with acids, which results in the decrease of photostability. To reduce this problem, the amines have been *N*-alkylated, *N*-alkoxylated, and *N*-acylated [13–15]. In a continuation of our ongoing program, we now report the synthesis and evaluation of new antioxidants **5a–f** that are derived from both 2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-ol (HTEMPO) and 2-(2-hydroxyphenyl)benzotriazole. These functionalities are generally considered to be thermal and photostable [16], and their basicity is low. In addition, nitroxide compounds have been used as topical antioxidants for many years [17–19]. The results of ultraviolet absorbance, thermogravimetric evaluation, and antioxidative properties are compared with those of the marketed photostabilizer HS-508.

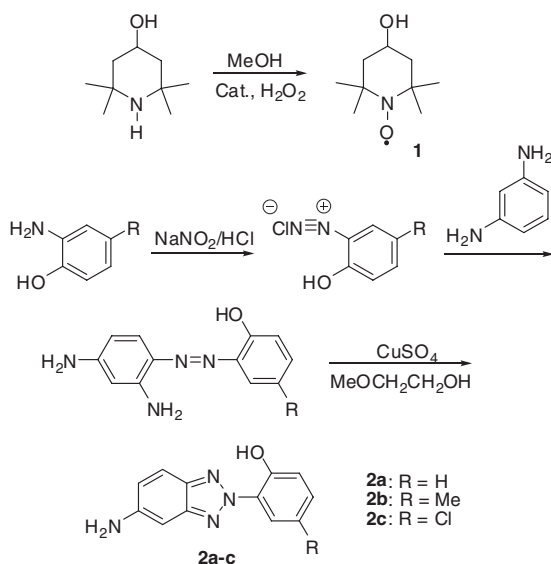


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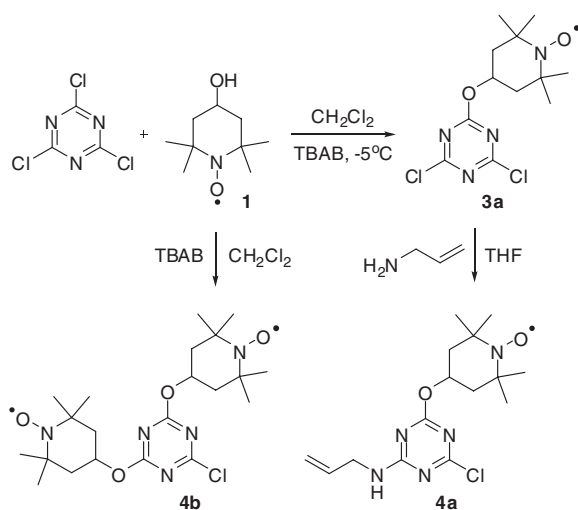
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Results and discussion

The synthetic routes to the desired products **5a–f** are shown in Schemes 1–3. They are self-explanatory.



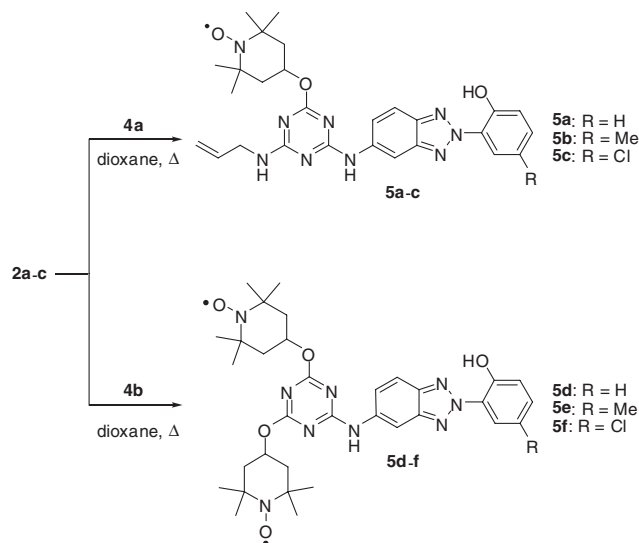
Scheme 1



Scheme 2

The synthesized products **5a–f** were characterized by their melting points, elemental analyses, and spectral methods. All analytical data fully support the given structures.

As shown in Figure 1, the ultraviolet-visible (UV-Vis) absorption bands of compounds **5a–f** are observed at 350–370 nm. Their absorption intensity is much greater than that of HS-508. In particular, the molar extinction coefficient of the target compounds, $2.10 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ (**5a**), $1.64 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ (**5b**), $2.04 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ (**5c**), $1.18 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ (**5d**), $1.49 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ (**5e**), and $1.56 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ (**5f**), are at least 3.7-fold greater than the value of $3.15 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ for HS-508.



Scheme 3

The results of the thermogravimetric tests are shown in Figure 2. Upon heating a significant mass loss is observed at temperatures higher than 170°C for HS-508, but compounds **5a–f** are relatively stable up to 220°C. These results indicate that the thermal stability of compounds **5a–f** is much better than that of the marketed photostabilizer HS-508.

The influence of the new HALSs **5a–f** on the photostability of PE was investigated by using the simulated aging experiment [3, 20, 21]. The stability of PE in the absence (homo-PE) and presence of **5a–f** (PE-**5a–f**) and HS-508 (PE-HS-508) was analyzed according to the method evaluating the thermal stability of polyethylene pipe and tube fittings

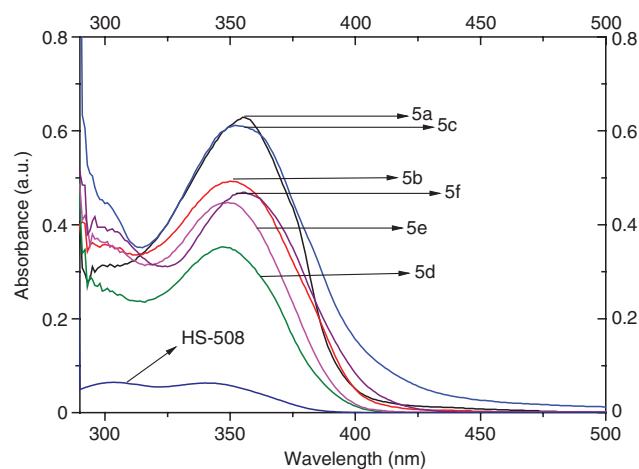


Figure 1: UV-Vis spectra of compounds **5a–f** and the reference stabilizer HS-508 in CHCl_3 ($c = 1.000 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) at room temperature.

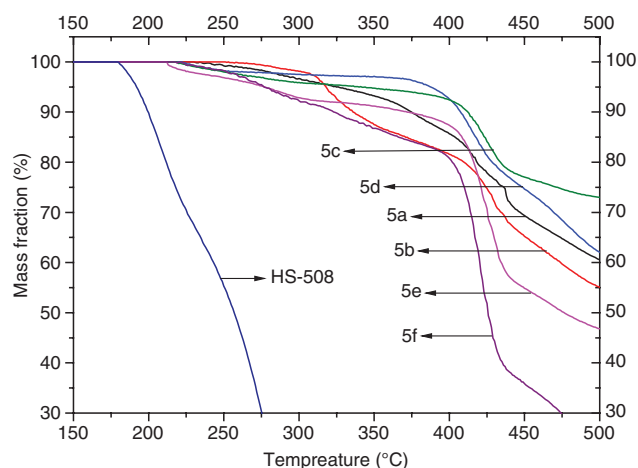


Figure 2: Results of a thermogravimetric analysis (TGA) test done at a temperature ranging from ambient to 500 °C under dry nitrogen. The heating rate was 20 °C min⁻¹.

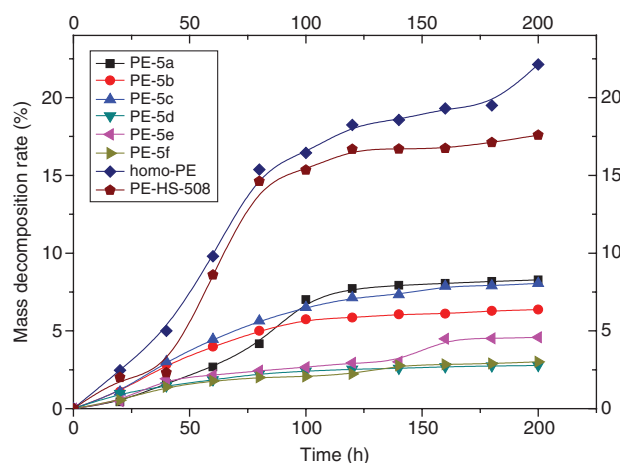


Figure 3: The mass loss rate of unaltered polyethylene (homo-PE) and in the presence of compounds **5a–f** and the reference antioxidant HS-508. The experiments were conducted in the fluorescence-UV light aging box.

(GB=T17391-1998, China). The obtained results are summarized in Figure 3. The mass decomposition rate of PE-**5a–f** is lower than that of homo-PE and PE-HS-508. It can also be seen that the photostability of **5d–f** (containing two nitroxyl radical groups) is much better than that of **5a–c** (containing only one nitroxyl radical group). These results demonstrate that the new HALSs show a good stabilizing effect.

Conclusion

Novel multifunctional nitroxyl radical hindered-amine photostabilizers **5a–f** were synthesized in good yield by

using an efficient methodology. Their UV-Vis absorption, thermal stability, and photostability were studied. The results indicate that the oxidation resistance and the photostabilization efficiency of the new stabilizers are much better than those of the marketed stabilizer HS-508.

Experimental

Cyanuric chloride, *m*-phenylenediamine, *o*-aminophenol, 2-amino-4-methylphenol, 2-amino-4-chlorophenol, allylamine, 2,2,6,6-tetramethylpiperidin-4-ol, and methyl trioctyl ammonium chloride (Aliquat336) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2-Hydroxyphenylbenzotriazole derivatives **2a–c** [12], 2-allylamino-4-(2,2,6,6-tetramethylpiperidin-*N*-oxyl-4-ol)-6-chloride-*s*-triazine **4a**, and 2,4-di(2,2,6,6-tetramethylpiperidin-*N*-oxyl-4-ol)-6-chloride-*s*-triazine **4b** were synthesized as previously described [22].

¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Varian INOVA spectrometer in CDCl₃. UV-Vis spectra were recorded on a Shimadzu UV-1700 UV-Vis spectrophotometer at room temperature in methanol. Thermogravimetric (TG) curves were recorded on Netzsch STA 449C TGA instrument from ambient temperature to 500 °C at a heating rate of 20 °C·min⁻¹ in dry nitrogen. IR spectra were measured with KBr pellets on a Perkin-Elmer 1600 FT-IR spectrometer at a 4-cm⁻¹ resolution. The aging test was conducted using a ZN-P aging box. Mass spectrometry was conducted with an Agilent AXIMA-CFR-plus MALDI-TOF-MS spectrometer. The reaction progress and the purity of the final products were followed by thin-layer chromatography on silica gel plates obtained from Sinopharm Chemical Reagent Co., Ltd. Elemental analysis was conducted with a Perkin-Elmer 240C instrument. The melting points were determined using an XT-4 melting point microscope without correction.

Synthesis of compound 1

Hydrogen peroxide (30%, 15.3 mL, 0.15 mol) was added dropwise at 65 °C to a mixture of 2,2,6,6-tetramethylpiperidine-4-ol (1.57 g, 0.1 mol) and iron(II) phthalocyanine (0.02 mol) in methanol (40 mL). The mixture was heated under reflux for 7 h then cooled to room temperature and filtered. The filtrate was concentrated *in vacuo*, and the residue was crystallized from chlorobenzene to yield orange crystals, mp 66–68 °C (lit. mp 68–70 °C [23]).

General procedure for synthesis of compounds **5a–f**

A mixture of 5-aminobenzotriazole derivative **2a–c** (0.01 mol), **4a** or **4b**, and potassium carbonate (1.38 g, 0.01 mol) in dioxane (30 mL) was stirred for 4 h at 110 °C then cooled and poured into 50 mL of water. The precipitated product was filtered and crystallized from chlorobenzene to yield pure product **5a–f** as a pale yellow solid.

2-[2-(2-Hydroxy)benzotriazol-5-amino]-4-allylamino-6-(2,2,6,6-tetramethylpiperidin-*N*-oxyl-4-ol)-*s*-triazine (5a**)** Yield 45%; mp 159–161 °C; ¹H NMR: δ 1.26 (s, 6H, piperidine 2×CH₃), 1.29 (s, 6H,

piperidine $2 \times \text{CH}_2$), 2.22 (d, $J = 8.8$ Hz, 4H, piperidine $2 \times \text{CH}_2$), 3.79 (d, $J = 6.8$ Hz, 2H, allyl CH_2), 5.12–5.41 (m, 1H, piperidine CH), 7.09–7.13 (m, H, =CH-), 7.19 (d, $J = 8.1$ Hz, 2H, $\text{CH}_2=$), 7.26–8.40 (m, 7H, Ar-H), 8.63 (br. s, 1H, NH), 9.35 (br. s, 1H, NH); ^{13}C NMR: δ 20.6, 44.5, 49.0, 59.4, 60.1, 104.3, 115.2, 117.1, 117.7, 119.3, 120.5, 123.9, 132.1, 135.2, 140.3, 144.6, 147.7, 151.6, 172.7; FT-IR: 698, 754, 1357, 1495, 1570, 1661, 2973, 3350 cm^{-1} ; ESI-HRMS. Calcd for $(\text{M}+\text{Na})^+$: m/z 553.2590. Found: m/z 553.2526. Anal. Calcd for $\text{C}_{27}\text{H}_{32}\text{N}_9\text{O}_3$: C, 61.12; H, 6.08; N, 23.76. Found: C, 61.20; H, 6.01; N, 23.88.

2-[2-(5-Methyl-2-hydroxyphenyl)benzotriazol-5-amino]-N-allylamino-6-(2,2,6,6-tetramethylpiperidin-N-oxyl-4-ol)-s-triazine (5b) Yield 48%; mp 168–169°C; ^1H NMR: 1.33 (s, 12H, piperidine $4 \times \text{CH}_2$), 1.54 (d, $J = 11.2$ Hz, 4H, piperidine $2 \times \text{CH}_2$), 2.87 (s, 3H, CH_3), 4.05 (d, $J = 6.8$ Hz, 2H, allyl CH_2), 5.05–5.16 (m, 1H, piperidine CH), 7.09–7.14 (m, H, =CH-), 7.22 (d, $J = 8.4$ Hz, 2H, $\text{CH}_2=$), 7.39–8.62 (m, 6H, Ar-H), 8.65 (br. s, 1H, NH), 9.54 (br. s, 1H, NH); FT-IR: 661, 751, 1350, 1469, 1577, 1637, 2964, 3227, 3356 cm^{-1} ; ESI-HRMS. Calcd for $(\text{M}+\text{Na})^+$: m/z 544.2761. Found: m/z 544.2785. Anal. Calcd for $\text{C}_{28}\text{H}_{34}\text{N}_9\text{O}_3$: C, 61.75; H, 6.29; N, 23.15. Found: C, 61.69; H, 6.24; N, 23.26.

2-[2-(2-Hydroxy-5-chlorophenyl)benzotriazol-5-amino]-N-allylamino-6-(2,2,6,6-tetramethylpiperidin-N-oxyl-4-ol)-s-triazine (5c) Yield 49%; mp 176–177°C; ^1H NMR: 1.34 (s, 12H, piperidine $4 \times \text{CH}_2$), 1.63 (d, $J = 7.1$ Hz, 4H, piperidine $2 \times \text{CH}_2$), 4.42 (d, $J = 11.8$ Hz, 2H, allyl CH_2), 5.12–5.24 (m, 1H, piperidine CH), 7.07 (m, H, =CH-), 7.21 (d, $J = 8.8$ Hz, 2H, $\text{CH}_2=$), 7.42–8.34 (m, 6H, Ar-H), 8.42 (br. s, 1H, NH), 9.37 (br. s, 1H, NH); FT-IR: 628, 729, 1350, 1495, 1578, 1637, 2966, 3226, 3351 cm^{-1} ; ESI-HRMS. Calcd for $(\text{M}+\text{Na})^+$: m/z 564.2210. Found: m/z 564.2238. Anal. Calcd for $\text{C}_{27}\text{H}_{31}\text{N}_9\text{O}_3\text{Cl}$: C, 57.39; H, 5.53; N, 22.31. Found: C, 57.52; H, 5.43; N, 22.40.

[2-(2-Hydroxy)benzotriazol-5-amino]-4,6-di(2,2,6,6-tetramethylpiperidin-N-oxyl-4-ol)-s-triazine (5d) Yield 52%; mp 155–157°C; ^1H NMR: δ 1.26 (s, 24H, piperidine $8 \times \text{CH}_2$), 1.72 (d, $J = 8.2$ Hz, 8H, piperidine $4 \times \text{CH}_2$), 2.47 (br. s, 1H, NH), 3.85–4.31 (m, 1H, piperidine CH), 6.88–8.28 (m, 7H, Ar-H); ^{13}C NMR: δ 20.4, 44.5, 57.5, 59.9, 105.3, 115.4, 117.2, 119.4, 120.4, 124.3, 135.5, 146.7, 151.6, 173.3; FT-IR: 628, 754, 1356, 1552, 1577, 1637, 2929, 3238, 3358 cm^{-1} ; ESI-HRMS. Calcd for $(\text{M}+\text{Na})^+$: m/z 668.3280. Found: m/z 668.3285. Anal. Calcd for $\text{C}_{33}\text{H}_{43}\text{N}_9\text{O}_5$: C, 61.38; H, 6.71; N, 19.52. Found: C, 61.45; H, 6.62; N, 19.39.

2-[2-(2-Hydroxy-5-methylphenyl)benzotriazol-5-amino]-4,6-di(2,2,6,6-tetramethylpiperidin-N-oxyl-4-ol)-s-triazine (5e) Yield 49%; mp 157–159°C; ^1H NMR: 1.12 (s, 24H, piperidine $8 \times \text{CH}_2$), 1.72 (s, 3H, CH_3), 1.91 (d, $J = 11.8$ Hz, 8H, piperidine $4 \times \text{CH}_2$), 3.85–4.31 (m, 2H, $2 \times$ piperidine CH), 5.12 (br. s, 1H, NH), 6.78–8.29 (m, 7H, Ar-H); FT-IR: 812, 1354, 1576, 1577, 1637, 2932, 2969, 3345 cm^{-1} ; ESI-HRMS. $(\text{M}+\text{Na})^+$: Calcd for $(\text{M}+\text{Na})^+$: m/z 718.2590. Found: m/z 718.2635. Anal. Calcd for $\text{C}_{34}\text{H}_{45}\text{N}_9\text{O}_5$: C, 61.89; H, 6.87; N, 19.11. Found: C, 61.78; H, 7.01; N, 19.18.

2-[2-(2-Hydroxy-5-chlorophenyl)benzotriazol-5-amino]-4,6-di(2,2,6,6-tetramethylpiperidin-N-oxyl-4-ol)-s-triazine (5f) Yield 48%; mp 166–167°C; ^1H NMR: 1.19 (s, 24H, piperidine $8 \times \text{CH}_2$), 1.93 (d, $J = 12$ Hz, 8H, piperidine $4 \times \text{CH}_2$), 3.84–4.31 (m, 2H, $2 \times$ piperidine CH), 5.23 (br. s, 1H, NH), 6.77–8.18 (m, 7H, Ar-H); FT-IR: 820, 1125, 1354, 1578, 1637, 2970, 3362 cm^{-1} ; ESI-HRMS. Calcd for $(\text{M}+\text{Na})^+$: m/z 698.3150. Found: m/z 698.3181. Anal. Calcd for $\text{C}_{33}\text{H}_{42}\text{N}_9\text{O}_5\text{Cl}$: C, 58.27; H, 6.22; N, 18.53. Found: C, 58.12; H, 6.15; N, 18.64.

Preparation of mixtures of polyethylene with photostabilizers

A mixture of polyethylene and photostabilizer (0.5–1.0% w/w) was heated to 150°C and stirred until a homogeneous solution was obtained, from which molding samples were obtained for simulated aging experiments.

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