## Xiaofeng Gou\*, Dong Liu, Chengwen Hua, Junlong Zhao and Wen Zhang Synthesis and properties of multifunctional hindered amine light stabilizers

**Abstract:** A series of multifunctional hindered amine light stabilizers (HALSs) for monomers were designed and synthesized from cyanuric chloride, allylamine, 2,2,6,6-tetramethylpiperidine-4-ol or 1,2,2,6,6-pentamethylpiperidine-4-ol, and 2-(2-hydroxyphenyl)-1,2,3-benzo-triazole derivatives through nucleophilic substitution. The new stabilizers were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR, ESI-HRMS and elemental analysis. The synthesized compounds **5a–f** were evaluated for their antioxidant and anti-aging properties. The results indicate that the new HALSs can considerably improve polymer photostability.

**Keywords:** HALSs; 2-(2-hydroxyphenyl)-1,2,3-benzotriazole; photostability; *s*-triazine; 2,2,6,6-tetramethylpiperidine; UV absorber.

## Introduction

The polymeric materials exposed to sunlight undergo degradation which decreases the use value and shortens their service life, mainly by photooxidation. The inherent characteristic and appearance of polymer materials may be weakened as a result of photodegradation [1–3]. Hence, polymeric auxiliaries are being studied and analyzed.

Hindered amine light stabilizers (HALSs) are one of the most important thermal/light stabilizing agents of polymeric materials. They are widely available with low toxicity and low cost, and they have excellent compatibilities with a broad range of commercially significant polymeric materials. HALSs have a good photostabilizing effect on organic materials, which may be 2–4 times higher than that of ultraviolet stabilizers [4, 5]. In general, HALSs are applied with other antioxidants and ultraviolet absorbers (UVAs). However, these two groups differ in their action, although both are classified as photodegradation stabilizers [6–8]. HALSs inhibit the processes of autoxidation by transformation of the parent amines to nitroxide radicals either by reaction with peroxy radicals or occasionally by reaction with singlet oxygen. The nitroxide radicals stop oxidative degradation by coupling of alkyl radicals [9, 10]. In contrast to 2,2,6,6-tetramethylpiperidines, 2-(2-hydroxyphenyl)-1,2,3-benzotriazole derivatives belong to UVAs [11]. They are transparent to visible light and are assumed to dissipate the absorbed energy in a harmless manner, that is, by converting the absorbed photon energy into heat without being chemically affected. If basic HALSs, benzotriazole and polymerizable allyl group fragments are linked through s-triazine ring in one molecule, this could result in a new stabilizer type with combined stabilizing effect. These moieties may display a synergistic effect in one molecule [12-15]. Bojinov and co-workers have synthesized several bifunctional HALSs linked to polymerizable monomers [16–19].

This paper describes the synthesis of compounds **5a**–**f** composed of multifunctional HALSs, a benzotriazole group, a polymerizable allyl group and a flame-retardant triazine moiety. UV-Vis absorption and thermal stability of these stabilizers were studied. Their influence on the photostability of copolymers has been investigated.

### **Results and discussion**

The synthetic routes are shown in Schemes 1–3. All reactions were monitored by TLC on silica gel and the synthesized products **2a,b, 3a,b, 4a–c** and **5a–f** were characterized by melting points, elemental analyses, FT-IR, ESI-HRMS and <sup>1</sup>H NMR spectra. All analytical data are in agreement with the desired structures.

Photostabilization efficiency, oxidation resistance and miscibility with polymeric materials (PE and PP) of compounds **5a–f** were studied. The results indicate that the solubility of new compounds **5a–f** is better than that for the previously reported compounds by Bojinov and co-workers [16–19]. The miscibility was evaluated by using the smooth degree (S). The miscibility of the new stabilizers is 0.63, whereas it is 0.51 for the previously reported compounds. The analysis of the results shows that the compounds have considerably high photostabilizing efficiency.

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Scheme 2

As shown in Figure 1, the absorption bands of compounds **5a–f** are observed at 300–350 nm. Their absorption intensity is higher than that of the HALS HS-508. And the maximum molar extinction coefficients of the title compounds are  $9.28 \times 10^4$  L/mol·cm<sup>-1</sup> (**5a**),  $3.63 \times 10^4$  L/mol·cm<sup>-1</sup> (**5b**),  $1.00 \times 10^5$  L/mol·cm<sup>-1</sup> (**5c**),  $5.78 \times 10^4$  L/mol·cm<sup>-1</sup> (**5d**),  $4.06 \times 10^4$  L/mol·cm<sup>-1</sup> (**5e**) and  $3.29 \times 10^4$  L/mol·cm<sup>-1</sup> (**5f**), but for HS-508, the coefficient is  $3.15 \times 10^4$  L/mol·cm<sup>-1</sup>. The results of TGA tests are shown in Figure 2 with a significant mass loss observed between 203°C and 254°C.

To investigate the influence of the monomers 5a-f on the photostability of the copolymers, the copolymers were tested by the simulated aging experiment [20–22]. The antioxidation property of the copolymers poly(MMA-co-stabilizers 5a-f) were tested and compared with the



### Conclusion

In this work, the multifunctional HALSs **5a–f** were synthesized in good yields by using an efficient and convenient



Scheme 3



**Figure 1** UV-Vis spectra of compounds **5a**–**f** and the reference stabilizer HS-508 in methanol ( $c=2.000\times10^{-4} \text{ mol/L}$ ) at room temperature.



Figure 2 Results of the TGA test done over a temperature range from ambient to 500°C with a heating rate of 20°C/min in dry nitrogen.



Figure 3 The antioxidation properties of the copolymers poly(MMAco-stabilizers 5a-f) as tested in the fluorescence-UV light aging box.

method. Their UV-vis absorption, thermal stability and photostability were studied. The results indicate that the oxidation resistance and photostabilization efficiency of the new stabilizers are better in comparison to the marketed stabilizer HS-508 in MMA.

## **Experimental**

Cyanuric chloride, *m*-phenylenediamine, *o*-aminophenol, 2-amino-4-methylphenol, 2-amino-4-chlorophenol, allylamine, 2,2,6,6-tetramethylpiperidin-4-ol (**1a**) and methyl trioctyl ammonium chloride (Aliquat 336) were purchased from Sinopharm Chemical Reagent Co., Ltd. 1,2,2,6,6-Pentamethylpiperidine-4-ol (**1b**) was synthesized and purified as previously described [23, 24]. The 2-hydroxyphenylbenzotriazole derivatives **4a–c** [25] were synthesized as previously described.

<sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on a Varian INOVA spectrometer in CDCl, and acetone-d. UV-Vis spectra were recorded on a Shimadzu UV-1700 ultravioletvisible spectrophotometer with 2 nm resolution, at room temperature in methanol. TG curves were recorded on an Netzsch STA 449C TGA instrument from ambient temperature to 500°C at a heating rate of 20°C/min in dry nitrogen. IR spectra were taken on a Perkin-Elmer 1600 FT-IR spectrometer in KBr pellets. Aging performance was tested on a ZN-P fluorescence-UV light aging box. Mass spectrometry was carried out with an Agilent AXIMA-CFR-plus MALDI-TOF mass spectrometer. The reaction course and purity of the final products were followed by TLC on silica gel (Sinopharm Chemical Reagent Co., Ltd.,  $F_{60}$ 254 20 × 20, 0.2 mm). Elemental analysis was carried out with a Perkin-Elmer 240C instrument. Melting points were determined using a XT-4 melting point microscope without correction.

#### General procedure for synthesis of compounds 3a-b

A mixture of 2,2,6,6-tetramethylpiperidin-4-ol **1a**, **b** (0.01 mol), finely ground sodium hydroxide (2.5 equiv.) and Aliquat 366 (0.04 g, 0.1 mmol) in toluene (30 mL) was stirred for 10 min. Then a solution of cyanuric chloride (1.84 g, 0.01 mol) in 20 mL of toluene was added at 0°C dropwise with vigorous stirring over a period of 30 min. The reaction process was monitored by TLC with methanol/ethyl acetate (1:5, V/V) as the eluent. After 4 h of stirring under the same conditions, the mixture was diluted in 25 mL of water before separation of the organic layer. The organic solution was washed with saturated solution of sodium chloride ( $\times$  3), dried over anhydrous sodium sulfate. This solution contained 2-(2,2,6,6-tetramethylpiperidin-4-oxy)-4,6-dichloro-s-triazine **2a,b.** Mp was 123.9–125.4°C for compound **2a** (lit. mp 125–126°C [26, 27]).

A solution of allylamine (0.57 g, 0.01 mol) in toluene (20 mL) was added dropwise under vigorous stirring at 40°C to a mixture of the intermediate **2a,b** (1 equiv.) in toluene (20 mL) and anhydrous potassium carbonate (1 equiv.) over a period of 30 min under dry nitrogen. After 3 h of stirring at 40°C, the reaction mixture was cooled to room temperature. The organic phase was filtered and concentrated *in vacuo* to yield a pale yellow residue. Chromatography on silica gel methanol/ethyl acetate (1:7) gave **3a,b** as a white solid.

**2-Allylamino-4-(2,2,6,6-tetramethylpiperidin-4-yloxy)-6-chloro-s-triazine (3a)** Yield 62%; mp 157.2–160.0°C; <sup>1</sup>H NMR (CDCl<sub>2</sub>):  $\delta$  1.21 (s, 6H, piperidine 2 × CH<sub>3</sub>), 1.29 (s, 6H, piperidine 2 × CH<sub>3</sub>), 1.55 (br s, 1H, piperidine NH), 2.09 (d, *J* = 12.0 Hz, 4H, piperidine 2 × CH<sub>2</sub>), 4.08 (d, *J* = 5.2 Hz, 2H, allyl CH<sub>2</sub>), 5.12–5.27 (m, H, piperidine CH), 5.42 (d, *J* = 10.0 Hz, 2H, CH<sub>2</sub>=), 5.87–5.92 (m, H, -CH=), 6.27 (br s, 1H, allyl NH); ESI-HRMS, m/z, (M+H<sup>+</sup>): Calcd 326.1737, observed 326.1748. Anal. Calcd for C<sub>15</sub>H<sub>24</sub>N<sub>5</sub>OCI: C, 55.29; H, 7.42; N, 21.49. Found: C, 55.34; H, 7.38; N, 21.41.

**2-Allylamino-4-(1,2,2,6,6-pentamethylpiperidine-4-yloxy)-6-chloro-s-triazine (3b)** Yield 60%; mp 136.4–138.1°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.11 (s, 6H, piperidine 2 × CH<sub>3</sub>), 1.19 (s, 6H, piperidine 2 × CH<sub>3</sub>), 2.15 (d, *J* = 11 Hz, 4H, piperidine 2 × CH<sub>2</sub>), 2.27 (s, 3H, CH<sub>3</sub>-N), 4.09 (d, *J* = 5 Hz, 2H, allyl CH<sub>2</sub>), 5.17–5.27 (m, H, piperidine CH), 5.28 (d, *J* = 7.0 Hz, 2H, CH<sub>2</sub>=), 5.80–5.91 (m, H, -CH=), 6.24 (br s, 1H, allyl NH); ESI-HRMS, m/z, (M+H<sup>+</sup>): Calcd 340.1901, observed 340.1904. Anal. Calcd for C<sub>16</sub>H<sub>26</sub>N<sub>5</sub>OCI: C, 56.54; H, 7.71; N, 20.61. Found: C, 56.50; H, 7.67; N, 20.53.

# General procedure for synthesis of compounds 4a-c

A solution of 0.01 mol o-aminophenol (2-amino-4-methylphenol or 2-amino-4-chlorophenol) in 15 mL of water and 2 mL of concentrated hydrochloric acid was diazotized at 0-5°C in the presence of 0.04 g of copper(II) sulfate pentahydrate with a solution of sodium nitrite (1 equiv.) in 5 mL of water. The cold solution (5°C) of the diazonium chloride was added dropwise to a solution (5°C) of *m*-phenylenediamine (1.08 g. 0.01 mol) in 20 mL of water and 1 mL of concentrated hydrochloric acid over a period of 20 min. To this mixture, a solution of sodium acetate (10 mL, 40%) was added over a period of 0.5 h with stirring at 5°C. After 2 h of stirring at room temperature, the reaction mixture was treated with 5 mL of 25% aqueous ammonium hydroxide solution (to pH = 8) and the precipitate of dark-red azo compound was isolated by filtration and washed four times with water. Then the dark-red azo compound was dissolved in 2-methoxyethanol (50 mL). Copper(II) sulfate pentahydrate (6.0 g) in 15 mL of water and 24 mL of 25% aqueous ammonium hydroxide solution were added with stirring to the solution of the azo compound. After 2 h at 98°C, the reaction mixture was cooled to room temperature. The suspension was filtered and the residue was stirred with 20 mL of 5 N hydrochloric acid for 1 h. To the resulting acid mixture, 10 mL of water and 6 mL of 25% aqueous ammonium hydroxide solution were added (to pH = 8). The crude precipitated product was isolated by filtration, washed with water and dried. Three-fold crystallization from butyl acetate afforded the substituted 5-aminobenzotriazole 4a-c as colorless needles.

**2-(5-Amino-2H-benzotriazol-2-yl)phenol (4a)** Yield 81%; mp 210.5–212.7°C (lit. mp 212–215°C [28]); 'H NMR (CDCl<sub>3</sub>): δ 4.02 (br s, 2H, NH<sub>2</sub>), 6.93–8.30 (m, 7H, ArH), 11.40 (br s, H, OH); ESI-HRMS, m/z, (M+H<sup>+</sup>): Calcd 227.0938, observed 227.0933). Anal. Calcd for  $C_{12}H_{10}N_4O$ : C, 63.71; H, 4.46; N, 24.76. Found: C, 63.67; H, 4.52; N, 24.81.

**2-(5-Amino-2H-benzotriazol-2-yl)-4-methylphenol** (4c) Yield 76%; mp 222.4–223.8°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.05 (s, 2H, NH<sub>2</sub>), 6.90–8.31 (m, 6H, ArH), 11.37 (s, H, OH); ESI-HRMS, m/z, (M+H<sup>+</sup>): Calcd 241.1093, observed 241.1089. Anal. Calcd for C<sub>12</sub>H<sub>9</sub>N<sub>4</sub>OCl: C, 55.29; H, 3.48; N, 21.49. Found: C, 55.36; H, 3.52; N, 21.61.

## General procedure for synthesis of compounds 5a-f

To a solution of 5-aminobenzotriazole derivative 4a-c (0.01 mol) in 30 mL of glacial acetic acid were added 0.082 g (0.01 mol) of sodium acetate and 0.01 mol of allylaminotriazinylpiperidine **3a,b**. The resulting mixture was stirred for 2 h at 120°C and then after cooling poured into 50 mL of water. The crude precipitated product was isolated by filtration and purified using column chromatography on silica gel eluting with methanol/ethyl acetate/triethylamine (2:16:1) to give **5a–f** as a pale yellow solid.

**2-[2-(2-Hydroxyphenyl)benzotriazol-5-amino]-4-allylamino-6-(2,2,6,6-tetramethylpiperidin-4-yloxy)-s-triazine** (5a) Yield 69%; mp 225.1–227.6°C; <sup>1</sup>H NMR (acetone- $d_6$ ):  $\delta$  1.26 (s, 12H, piperidine 4 × CH<sub>3</sub>), 1.61 (d, *J* = 7.1 Hz, 4H, piperidine 2 × CH<sub>2</sub>), 2.02 (br s, 1H, piperidine NH), 4.1 2(d, *J* = 7 Hz, 2H, allyl CH<sub>2</sub>), 5.13–5.30 (m, 1H, piperidine CH), 7.09–7.13 (m, H, =CH-), 7.19 (d, *J* = 8 Hz, 2H, CH<sub>2</sub>=), 7.26–8.39 (m, 7H, ArH), 8.63 (br s, 1H, NH), 9.55 (br s, 1H, NH), 11.15 (br s, 1H, OH); <sup>13</sup>C NMR (acetone- $d_6$ ),  $\delta$  (ppm): 24.3, 44.9, 49.1, 59.6, 60.3, 103.8, 104.7, 118.1, 118.4, 119.7, 122.7, 124.7, 127.1, 130.9, 138.2, 140.5, 144.0, ESI-HRMS, m/z, (M+H<sup>+</sup>): Calcd 516.2826, observed 516.2835. Anal. Calcd for C<sub>27</sub>H<sub>33</sub>N<sub>9</sub>O<sub>2</sub>: C, 62.89; H, 6.45; N, 24.45. Found: C, 63.01; H, 6.38; N, 24.61.

**2-[2-(2-Hydroxyphenyl)benzotriazol-5-amino]-4-allylamino-6-(1,2,2,6,6-pentamethylpiperidin-4-yloxy)-s-triazine (5b)** Yield 63%; mp 235.2–236.9°C; 'H NMR (acetone- $d_{o}$ ):  $\delta$  1.39 (s, 12H, piperidine 4 × CH<sub>3</sub>), 1.54 (d, J = 7 Hz, 4H, piperidine 2 × CH<sub>2</sub>), 2.07 (s, 3H, CH<sub>3</sub>-N), 4.07 (d, J = 7 Hz, 2H, allyl CH<sub>2</sub>), 4.11–4.33(m, 1H, piperidine CH), 7.10–7.14 (m, H, =CH-), 7.19 (d, J = 8 Hz, 2H, CH<sub>2</sub>=), 7.39–8.35 (m, 7H, ArH), 8.62 (br s, 1H, NH), 9.63 (br s, 1H, NH), 11.14 (br s, 1H, OH); FT-IR, v/cm<sup>3</sup>: 682, 750, 1247, 1491, 1583, 1660, 2925, 3677; ESI-HRMS, m/z, (M+H<sup>+</sup>): Calcd 530.3029, observed 530.2992. Anal. Calcd for C<sub>28</sub>H<sub>35</sub>N<sub>9</sub>O<sub>2</sub>: C, 63.50; H, 6.66; N, 23.80. Found: C, 63.34; H, 6.72; N, 23.86.

**2-[2-(5-Methyl-2-hydroxyphenyl)benzotriazol-5-amino]-4-allylamino-6-(2,2,6,6-tetramethylpiperidin-4-yloxy)-s-triazine** (5c) Yield 70%; mp 221.3–224.5°C; <sup>1</sup>H NMR (acetone- $d_c$ ):  $\delta$  1.23 (s, 12H, piperidine 4 × CH<sub>3</sub>), 1.44 (d, *J* = 9 Hz, 4H, piperidine 2 × CH<sub>2</sub>), 2.05 (br s, 1H, piperidine NH), 2.83 (s, 3H, CH<sub>3</sub>), 4.09 (d, *J* = 7 Hz, 2H, allyl CH<sub>2</sub>), 5.12–5.26 (m, 1H, piperidine CH), 7.09–7.14 (m, H, =CH-), 7.22 (d, *J* = 8 Hz, 2H, CH<sub>2</sub>=), 7.39–8.62 (m, 6H, ArH), 8.65 (br s, 1H, NH), 9.54 (br s, 1H, NH), 10.93 (br s, 1H, OH); FT-IR, v/cm<sup>1</sup>: 684, 814, 1246, 1284, 1511, 1663, 2858, 3614; ESI-HRMS, m/z, (M+H<sup>+</sup>): Calcd 530.3030, observed 530.2992. Anal. Calcd for  $C_{28}H_{35}N_9O_2$ : C, 63.50; H, 6.66; N, 23.80. Found: C, 63.58; H, 6.44; N, 23.73.

**2-[2-(5-Methyl-2-hydroxyphenyl)benzotriazol-5-amino]-4-allylamino-6-(1,2,2,6,6-pentamethylpiperidin-4-yloxy)-s-triazine** (5d) Yield 65%; mp 216.4–218.5°C; <sup>1</sup>H NMR (acetone- $d_{o}$ ):  $\delta$  1.23 (s, 12H, piperidine 4 × CH<sub>3</sub>), 1.44 (d, *J* =9.1 Hz, 4H, piperidine 2 × CH<sub>2</sub>), 2.05 (br s, 1H, piperidine NH), 2.83 (s, 3H, CH<sub>3</sub>), 4.09 (d, *J* = 7 Hz, 2H, allyl CH<sub>2</sub>), 5.12–5.26 (m, 1H, piperidine CH), 7.09 (m, H, =CH-), 7.22 (d, *J* = 8.4 Hz, 2H, CH<sub>2</sub>=), 7.37–8.60 (m, 6H, ArH), 8.62 (br s, 1H, NH), 9.54 (br s, 1H, NH), 10.93 (br s, 1H, OH); FT-IR, v/cm<sup>-1</sup>: 684, 814, 1246, 1284, 1511, 1663, 2858, 3614; ESI-HRMS, m/z, (M+H<sup>+</sup>): Calcd 544.3183, observed 544.3148. Anal. Calcd for C<sub>29</sub>H<sub>37</sub>N<sub>9</sub>O<sub>2</sub>: C, 64.07; H, 6.86; N, 23.19. Found: C, 63.14; H, 6.72; N, 23.11.

**2-[2-(2-Hydroxy-5-chlorophenyl)benzotriazol-5-amino]-4-allylamino-6-(2,2,6,6-tetramethylpiperidin-4-yloxy)-s-triazine** (5e) Yield 67.7%, mp 262.3–264.7°C. 'H NMR (acetone- $d_{c}$ ):  $\delta$  (ppm): 1.29 (s, 12H, piperidine 4 × CH<sub>3</sub>), 1.31 (d, *J* = 7 Hz, 4H, piperidine 2 × CH<sub>2</sub>), 2.01 (br s, 1H, piperidine NH), 4.31 (d, *J* = 7 Hz, 2H, allyl CH<sub>2</sub>), 5.12–5.24 (m, 1H, piperidine CH), 7.04 (m, H, =CH-), 7.21 (d, *J* = 9 Hz, 2H, CH<sub>2</sub>=), 7.42–8.34 (m, 6H, ArH), 8.62 (br s, 1H, NH), 9.57 (br s, 1H, NH), 11.18 (br s, 1H, OH); FT-IR, v/cm<sup>-1</sup>: 710, 817, 1244, 1283, 1505, 1658, 3272, 3676. ESI-HRMS, m/z, (M+H<sup>+</sup>): Calcd 550.2438, observed 550.2446. Anal. Calcd for C<sub>27</sub>H<sub>32</sub>N<sub>9</sub>O<sub>2</sub>Cl: C, 58.96; H, 5.86; N, 22.92. Found: C, 59.06; H, 5.91; N, 23.03.

### References

- Di, Z. C.; Lu, W. Z.; Wang, K. L.; Liang, J. Studies on UV transparent characteristics of carbon nanotube filled LDPE films. *Chem. J. Chinese Univ.* 2004, 25, 394–396.
- Butola, B. S.; Joshi, M. Photostability of HDPE filaments stabilized with UV absorbers (UVA) and light stabilizers (HALS).
   J. Eng. Fibers Fabrics 2013, 8, 61–68.
- [3] Evans, P. D.; Kraushaar, G. S.; Liu, C. L.; Cullis, L.; Sebe, G.
  <u>Photostabilization of wood using low molecular weight phenol</u> <u>formaldehyde resin and hindered amine light stabilizer</u>. *Polym. Degrad. Stabil.* 2013, *98*, 158–168.
- Yang, Y. C.; Cheng, J.; Cheng, C. M.; He, J.; Guo, B. H.; Zhao, Y. F. Design, synthesis and anti-oxidative evaluation of novel anti-oxidant molecules in polyolefin. *Chem. J. Chinese Univ.* 2011, *32*, 286–291.
- [5] Chen, W.; An, P.; Chen, Y. X.; Li, Y.; Yan, X. L.; Chen, L. G. <u>Synthesis and light-stabilizing ability of a series of hindered</u> piperidine derivatives. *Synth. Commun.* 2012, *42*, 1419–1425.
- [6] Chai, R. D.; Chen, S. J.; Zhang, J. Combined effect of hindered amine light stabilizer and ultraviolet absorbers on photodegradation of poly(vinyl chloride). J. Vinyl Addit. Technol. 2012, 18, 17–25.
- Bojinov, V. B. Synthesis of novel bifunctional hindered amine-UV absorber polymer stabilizers. *Polym. Degrad. Stabil.* 2006, *91*, 128–135.
- [8] Konstantinova, T.; Lazarova, R., Bojinov, V. On the photostability of some naphthalimide dyes and their copolymers with methyl methacrylate. *Polym. Degrad. Stabil.* 2003, *82*, 115–118.

**2-[2-(2-Hydroxy-5-chlorophenyl)benzotriazol-5-amino]-4-allylamino-6-(1,2,2,6,6-pentamethylpiperidin-4-yloxy)-s-triazine** (**5f**) Yield 62%; mp 267.3–270.7°C; <sup>1</sup>H NMR (acetone- $d_{o}$ ):  $\delta$  1.29 (s, 12H, piperidine 4 × CH<sub>3</sub>), 1.61 (d, J = 7.1 Hz, 4H, piperidine 2 × CH<sub>2</sub>), 2.85 (s, 3H, CH<sub>3</sub>-N), 4.16 (d, OH); FT-IR, v/cm<sup>-1</sup>: 713, 819, 1244, 1283, 1504, 1658, 3274, 3676; ESI-HRMS, m/z, (M+H<sup>+</sup>): Calcd 564.2593, observed 564.2602. Anal. Calcd for C<sub>28</sub>H<sub>34</sub>N<sub>9</sub>O<sub>2</sub>Cl: C, 59.62; H, 6.08; N, 22.35. Found: C, 59.52; H, 6.13; N, 22.40.

## General procedure for synthesis of polymers poly(MMA-co-stabilizer 5a-f)

The free-radical copolymerization of the monomeric stabilizers with methyl methacrylate (MMA) was investigated [29, 30]. A solution of MMA in toluene was added dropwise with stirring at 75°C to a mixture of 1.0 wt.-% of the corresponding HALS monomer, 1.0 wt.-% of azobisisobutyronitrile and 1.0 wt.-% of dibutyl phthalate (DBP) in a mixed solvent toluene/tetrahydrofuran ( $V_{toluene}$ : $V_{THF}$  = 7:3). The resulting mixture was polymerized for 8 h under a dry nitrogen atmosphere. This process was controlled by TLC analysis until the filtrate was free of monomer **5a–f**. Then the precipitated copolymers poly(MMA-co-stabilizer **5a–f**) were repeatedly washed with methanol and dried under reduced pressure to constant weight at room temperature.

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- [9] Gryn'ova, G.; Ingold, K. U.; Coote, M. L. New insights into the mechanism of amine/nitroxide cycling during the hindered amine light stabilizer inhibited oxidative degradation of polymers. J. Am. Chem. Soc. 2012, 134, 12979–12988.
- [10] Hodgson, J. L.; Coote, M. L. Clarifying the mechanism of the denisov cycle: how do hindered amine light stabilizers protect polymer coatings from photo-oxidative degradation macromolecules. *Macromolecules* 2010, 43, 4573–4583.
- [11] Katritzky, A. R.; Zhang, S. M.; Wang, M. Y.; Kolb, H. C.; Steel, P. J. Novel syntheses of polysubstituted pyrroles and oxazoles by 1,3-dipolar cycloaddition reactions of benzotriazolestabilized nitrile ylides. *J. Heterocycl. Chem.* 2002, *39*, 759–765.
- [12] Kruczala, K.; Aris, W.; Schlick, S. Stabilization and early degradation of UV-irradiated heterophasic propylene-ethylene copolymers based on ESR, ESR imaging, UV-vis and DSC: effect of ethylene content and UV wavelength. *Macromolecules* 2005, 38, 6979–6987.
- [13] Liu, X. X.; Chen, Y. L. Reactive-HALS I: synthesis, characterization, copolymerization reactivity and photo-stabilizing performance applied in UV-curable coatings. *Polym. Adv. Techn.* 2002, *13*, 247–253.
- [14] Cao, K.; Wu, S. L.; Qiu, S. L.; Li, Y.; Yao, Z. Synthesis of N-alkoxy hindered amine containing silane as a multifunctional flame retardant synergist and its application in intumescent flame retardant polypropylene. *Ind. Eng. Chem. Res.* 2013, *52*, 309–317.

- [15] Wang, Z.; Ning, P. S.; Ding, Z. M. The research progress of hindered amine light stabilizers. *Plast. Addit.* 2012, 1–9.
   DOI: 10.3969/j.issn.1672-6294.2012.01.001.
- Bojinov, V. B., Grabchevb, I. Synthesis of new combined
  2,2,6,6-tetramethylpiperidine 2-hydroxyphenylbenzotriazole
  1,3,5-triazine derivatives as stabilizers for polymers. *Polym. Degrad. Stabil.* 2001, 74, 543–550.
- [17] Bojinov, V. Synthesis and properties of adducts of a hindered amine and 2-hydroxyphenylbenzotriazole as novel polymer stabilizers. *Photochem. Photobiol. Sci.* 2002, 1, 340–346.
- Bojinov, V. B., Simeonov, D. B. Synthesis of novel bifunctional polymer stabilizers – a combination of HALS and UV absorber. *J. Photochem. Photobiol. A Chem.* 2006, 180, 205–212.
- [19] Bojinov, V. Synergistic efficiency of combined HALS-UV absorber polymerizable stabilizers. J. Appl. Polym. Sci. 2006, 102, 2408–2415.
- [20] Evans, P. D.; Gibsonb, S. K.; Cullis, L.; Liu, C. L.; Sebe, G. <u>Photostabilization of wood using low molecular weight phenol</u> <u>formaldehyde resin and hindered amine light stabilizer</u>. *Polym. Degrad. Stabil.* **2013**, *98*, 158–168.
- [21] Therias, S. Y.; Mailhot, B.; Gonzalez, D.; Gardette, J. L. Photooxidation of polypropylene/montmorillonite nanocomposites. *Chem. Mater.* 2005, 17, 1072–1078.
- [22] Bojinov, V.; Grabchev, I. Synthesis and properties of new adducts of 2,2,6,6-tetramethylpiperidine and 2-hydroxyphenylbenzotriazole as polymer photostabilizers. J. Photochem. Photobiol. A 2002, 150, 223–231.

- [23] Marc, G. C.; Mortsel, J. J.; Hove, W. J. UV-absorbing polymer latex. Patent US 3761272, 1971.
- [24] Liu, X.; Ju, C. X.; Hu, R. X.; Gu, D. P. Method of preparation of 4-hydroxy-1,2,2,6,6-pentamethylpiperidine. J. Hebei Normal Univ. (Natural Sci. Edn.) 2006, 30, 326–328.
- [25] Nakaya, F.; Noda, T.; Sakashita, K. Method of producing a polymer using monomers having a piperidine skeleton and molded body. *Patent WO 2011068110*, 2011.
- [26] Ren, X. H.; Jiang, Z. M.; Li, R. Preparation of halamine germicide for fabrics. *Patent CN 102797150*, 2012.
- [27] Bojinov, V.; Konstantinova, T.; Konstantinov, H. Synthesis and application of triazinyl-2,2,6,6-tetramethylpiperidine derivatives as stabilizers for polymeric materials. *Die Angew. Makromol. Chem.* **1998**, *260*, 17–20.
- [28] Refat, M. S. Synthesis, spectroscopic characterization, thermal, and photostability studies of 2-(2'-hydroxy-5'-phenyl)-5-aminobenzotriazole complexes. J. Therm. Anal. Calorim.
   2010, 102, 1095–1103.
- [29] Ma, W.; Meng, M.; Jiang, X.; Tang, B. T.; Zhang, S. F. Synthesis of a water-soluble macromolecular light stabilizer containing hindered amine structures. *Chinese Chem. Lett.* **2013**, *24*, 153–155.
- [30] Taguchi, Y.; Ishida, Y.; Ohtani, H.; Matsubara, H. Direct analysis of an oligomeric hindered amine light stabilizer in polypropylene materials by MALDI-MS using a solid sampling technique to study its photostabilizing action. *Anal. Chem.* 2004, 76, 697–703.