A Simple Synthetic Method of a 1,3,5-Triazine UV Absorbent CGL-479 and Its Characterization

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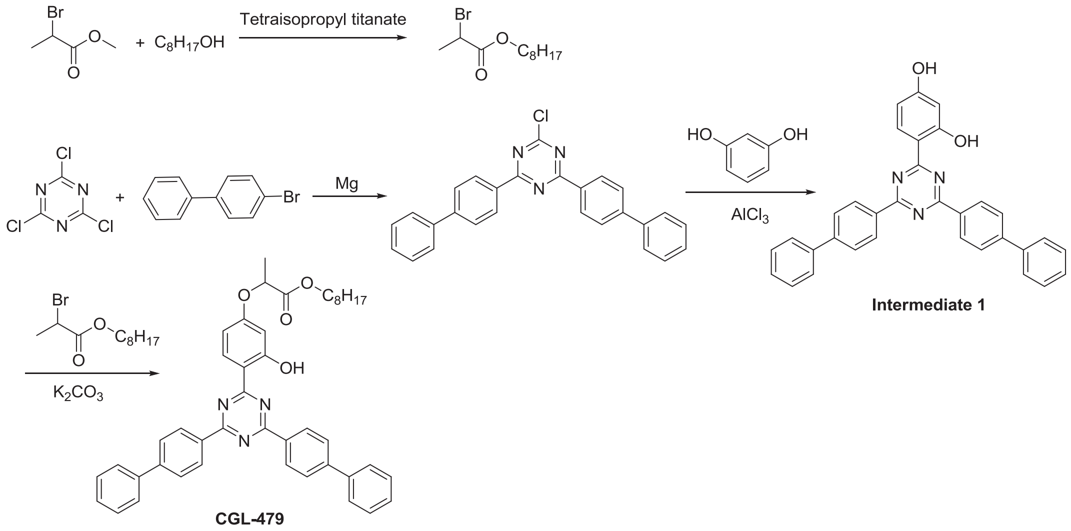

As a novel ultraviolet (UV) absorbent with excellent performance in UVA section (320 ~ 400 nm), 2-{2-hydroxy-4-[(octyloxycarbonyl)ethylideneoxy]phenyl}-4,6-Bis(4-biphenylyl)-1,3,5-triazine (CGL-479) was synthesized in a simple method with a total yield of 45.3% in four steps. Its outstanding UV absorption capability ($\lambda_{max} = 326$ nm, $\varepsilon_{max} = 4.15 \times 10^4$ L•mol^{-1}•cm^{-1}), high thermostability [T_5 (the temperature of losing 5% in weight) = 385 °C], and compatibility with polymer materials make it a potential substitute of the traditional UV absorbents.

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Satisfactory performance of paint coat for industrial and decorative applications has been successfully achieved in recent years. However, chemists are challenged with today's demand for novel light stabilizers with high performance, good quality, and low cost[1,2]. The UV absorbents, including Salicylate, Benzophenone, Benzotriazole and Triazine, are well-known effective light stabilizers[3–5]. However, these traditional UV absorbents are disadvantaged for their seemingly low thermostability, inferior photopermanence, high volatility, and poor compatibility with superpolymer[3–7]. Thus, substituted triazines were explored, and it was found that they exhibit superior properties as a novel UV absorbent. In addition to their advanced photopermanence and heat stability, substituted triazines show excellent chemical resistance without interaction with metals or strong alkalis[8–11].

Today, 1,3,5-triazine UV absorbents such as 2-[2-hydroxy-4-(hexyloxy)phenyl]-4,6-Bis(4-diphenylyl)-1,3,5-triazine (Tinuvin-1577), 2-(2-hydroxy-4-octyloxyphenyl)-4,6-Bis(2,4-dimethylphenyl)-1,3,5-triazine (Cyasorb-1164), and 2,4,6-Tri(2,4-dihydroxyphenyl)-1,3,5-triazine (Triazine-5) have been commercially available. Normally, an ideal UV absorbent should have an intensive absorption in UVA section (320 ~ 400 nm). However, the applications of the aforementioned 1,3,5-triazine UV absorbents are limited for their maximum absorption peak falls in the UVB section (290 ~ 320 nm)[12,13]. Hence, it is of practical significance to design and synthesize a novel substituted 1,3,5-triazine with a strong absorption in the UVA section.

Schaller *et al.* [3] reported the UV absorption capability of a novel 1,3,5-triazine compound 2-{2-hydroxy-4-[(octyloxycarbonyl)ethylideneoxy]phenyl}-4,6-Bis(4-biphenylyl)-1,3,5-triazine (CGL-479) in 2008, and it showed that CGL-479 has a sensational absorption capability in UVA section. Now it has been started to be widely used in the area of film industry [14–17] and liquid crystal display televisions[18–22]. So developing a convenient synthetic technology of CGL-479 is becoming more and more significant. In this paper, we synthesized CGL-479 with a simple method achieving a total yield of 45.3%. Besides, the CGL-479 is characterized with superior absorption ability, high thermostability [T_5 (the temperature of losing 5% in weight) = 385 °C], and good compatibility with polymer materials due to its reaction with polyester matrix to form the covalent bonds [14].

RESULTS AND DISCUSSION

Design and synthesis of CGL-479. Commercially available and widely used 1,3,5-triazine UV absorbents, such as Cyasorb-1164, have strong absorption in UVB section ($\lambda_{max} = 293$ nm, $\varepsilon_{max} = 3.35 \times 10^4$ L•mol^{-1}•cm^{-1}, CH_2Cl_2) and weak absorption in UVA section ($\lambda = 336$ nm, $\varepsilon = 1.95 \times 10^4$ L•mol^{-1}•cm^{-1}). To achieve an evident red shift of the maximum absorption peak into UVA section, the biphenyl group was introduced into the structure of CGL-479, resulting in a large conjugated system. A long alkoxy chain was imported to improve the thermostability and compatibility with polymer materials.

The synthesis route of CGL-479 was shown in Scheme 1. The process started with the preparation of 2-chloro-4,6-Bis (4-biphenylyl)-1,3,5-triazine, which was obtained by a Grignard reaction from cyanuric chloride and 4-bromobiphenyl, and then treated with resorcinol to afford the intermediate 1. Another intermediate Octyl 2-bromopropionate was prepared by the classical transesterification reaction from Methyl 2-bromopropionate and n-octanol. Condensation of intermediate 1 with Octyl 2-bromopropionate gave the compound CGL-479.

UV absorption properties of CGL-479. The UV absorption properties of CGL-479 and Cyasorb-1164 were comparatively studied in dichloromethane (DCM) which was dried with CaH_2. The test concentration of these two compounds was 3.5×10^{-5} M. The absorption spectra of CGL-479 exhibited a large red shift and a stronger absorption intensity ($\lambda_{max} = 326$ nm, $\varepsilon_{max} = 4.15 \times 10^4$ L•mol^{-1}•cm^{-1}) relative to that of Cyasorb-1164 ($\lambda_{max} = 293$ nm, $\varepsilon_{max} = 3.35 \times 10^4$ L•mol^{-1}•cm^{-1}), respectively (Figure 1). The maximum absorption peak also fell in the UVA section. These favorable variations were apparently attributable to the introduction of large conjugated systems.

Thermostability and compatibility properties of CGL-479. The thermostability of UV absorbents was one of the most significant indicators about the potential for industrial application. As shown in Figure 2, CGL-479 exhibited a higher thermostability than Cyasorb-1164, allowing for its wider applications. The T_5 and T_{50} were 385 °C and 470 °C for CGL-479, 368 °C and 448 °C for Tinuvin-1577 [12], and 330 °C and 395 °C for Cyasorb-1164, respectively.

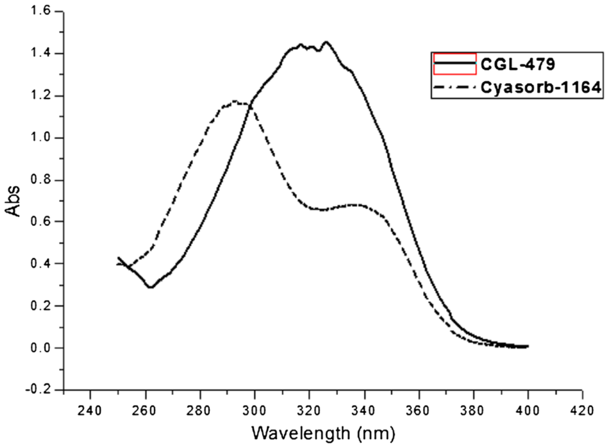
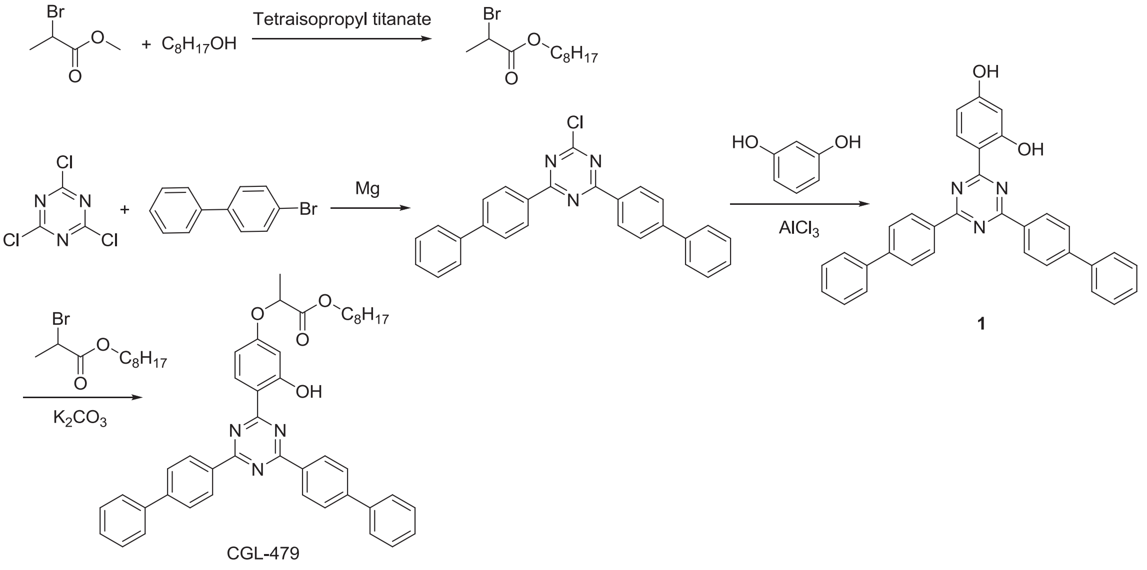


Figure 1. UV absorption spectra of CGL-479 and Cyasorb-1164 in DCM.

Scheme 1. The synthetic route of CGL-479



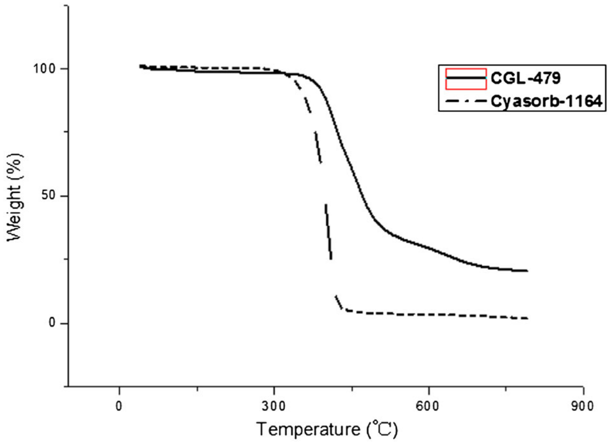


Figure 2. Thermogravimetric analysis spectra of CGL-479 and Cyasorb-1164. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Some of these traditional UV absorbents such as the Benzotriazoles have relatively low molecular weight, which would lead to the migration to the surface and volatilization during the machining process, resulting in the decrease of absorbents' density and protective effect. The introduction of a long alkoxy chain overcome this shortcoming and enabled CGL-479 to be homodispersed steadily.

In conclusion, a novel UV absorbent CGL-479 was synthesized in a simple synthetic method with a total yield of 45.3%. The CGL-479 exhibited perfect ultraviolet absorption ability in UVA section ($\lambda_{max} = 326$ nm, $\varepsilon_{max} = 4.15 \times 10^4$ L•mol^{-1}•cm^{-1}), high thermostability ($T_5 = 385\,°C$), and good compatibility with polymer materials. These unique advantages make it a potent substitute of traditional UV absorbents in industrial applications.

EXPERIMENTAL

General information. Reagents and solvents were obtained from commercial suppliers. Anhydrous tetrahydrofuran (THF) was distilled from sodium, and anhydrous o-dichlorobenzene was distilled from calcium hydride. All reactions were monitored by TLC (silica gel GF254s, QingdaoHaiyang). Column chromatography was performed by using 200–300 mesh silica gel. NMR spectra were recorded on Varian Inova-400 MHz NMR spectrometer with residual solvent peaks as an internal reference. MS were recorded on a LCQ Advanced MAX mass spectrometer. High Resolution Mass Spectrometry was measured on Varian QFT FTICR-MS spectrometer. IR spectra were recorded with KBr pellets on a Bruker-Tensor 27 spectrometer. UV-visible spectra were recorded on a Nicoet Evolution 300 spectrophotometer. Thermo gravimetric analyses were measured on a Q500 Thermo gravimetric analyzer. Melting points were observed on YRT-3 Melting Point Tester and uncorrected.

Octyl 2-bromopropionate. To a stirred n-octane (100 mL) in a 250 mL four-necked flask with Dean-Stark apparatus were added Methyl 2-bromopropionate (4.98 g, 30.0 mmol) and n-octanol (4.29 g, 33.0 mmol); the mixture was stirred for 1 h at 130 °C to remove water and then cooled to 80 °C. Tetraisopropyl titanate (0.43 g, 1.50 mmol) in 10 mL n-octane was added very slowly into the mixture and stirred for 0.5 h. The resulting mixture was firstly stirred at 110 °C for 1 h and then stirred for 8 h under reflux. After cooled to 80 °C, water (1 mL) was added with stirring. Filtered and the filtrate was washed with water (20 mL × 2). The organic layer was dried with anhydrous $MgSO_4$ and concentrated. The residue was purified by silica gel column (Petroleum, Rf = 0.6) to give Octyl 2-bromopropionate (6.86 g, 26.0 mmol) as a yellow liquid in a yield of 86.1%.

^{1}H NMR (400 MHz, CD_3OD) δ (ppm): 4.49 (q, $J = 6.9$ Hz, 1H), 4.24–4.11 (m, 2H), 1.80 (d, $J = 6.9$ Hz, 3H), 1.69 (td, $J = 13.3$, 6.6 Hz, 2H), 1.34 (d, $J = 3.3$ Hz, 10H), 0.93 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ (ppm): 171.66, 66.85, 41.28, 32.91, 30.29, 30.25, 29.49, 26.86, 23.67, 22.08, 14.50. MS (ESI) m/z: calcd. for $C_{11}H_{21}BrO_2$ 265.08 (positive ion), found 265.14 (positive ion).

2-chloro-4,6-Bis(4-biphenylyl)-1,3,5-triazine. To a stirred anhydrous THF (20 mL) under dry N_2 protection in a 100 mL four-necked flask were added magnesium (0.36 g, 15.0 mmol) and a bit of iodine; the mixture was stirred for 0.5 h at 55 °C. 4-bromobiphenyl (3.43 g, 15.0 mmol) in anhydrous THF (40 mL) was added very slowly into the mixture and was stirred for 2 h under reflux. After cooling down, the mixture was added dropwise into a 250 mL four-necked flask containing cyanuric chloride (1.08 g, 6.00 mmol) and anhydrous THF (100 mL) with stirring at 40 °C. The reaction mixture was stirred for 1 h at 50 °C. The solvent was evaporated under reduced pressure, water (100 mL) was added then extracted with CH_2Cl_2 (50 mL × 3). The organic phases were combined, dried with anhydrous $MgSO_4$, and concentrated. The residue was purified by silica gel column (DCM/Petroleum = 1:1, Rf = 0.6) to give 2-chloro-4,6-Bis(4-biphenylyl)-1,3,5-triazine (1.59 g, 3.80 mmol) as a white solid in a yield of 63.3%.

Melting point: 216–218 °C (lit. [11]: 217–220 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.19 (d, $J = 8.4$ Hz, 4H), 7.86 (d, $J = 8.4$ Hz, 4H), 7.77 (d, $J = 7.4$ Hz, 4H), 7.50 (t, $J = 7.5$ Hz, 4H), 7.42 (t, $J = 7.3$ Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 162.60, 153.63, 144.56, 138.63, 129.31, 129.20, 129.15, 128.56, 127.01, 126.83.

2-(2,4-dihydroxyphenyl)-4,6-Bis(4-biphenylyl)-1,3,5-triazine (Intermediate 1). To a stirred anhydrous o-dichlorobenzene (80 mL) under dry N_2 protection in a 250 mL four-necked flask were added 2-chloro-4,6-Bis(4-biphenylyl)-1,3,5-triazine (8.38 g, 20.0 mmol) and anhydrous $AlCl_3$ (6.00 g, 45.0 mmol); the mixture was stirred for 0.5 h at 25 °C. Then resorcinol (2.42 g, 22.0 mmol) was added, and the mixture was stirred for 2 h at 85 °C. After cooling down, ice water (80 mL) was added slowly, and o-dichlorobenzene was evaporated under reduced pressure. The mixture was filtered and washed with water (50 mL × 3); the filter cake was dried under vacuum for 3 h at 50 °C to give intermediate 1 (8.38 g, 17.0 mmol) as a yellow solid in a yield of 86.5%.

^{1}H NMR (400 MHz, DMSO) δ (ppm): 13.27 (s, 1H), 10.49 (s, 1H), 8.59 (d, $J = 8.3$ Hz, 4H), 8.50 (d, $J = 8.8$ Hz, 1H), 7.92 (d, $J = 8.3$ Hz, 4H), 7.78 (d, $J = 7.4$ Hz, 4H), 7.53 (t, $J = 7.4$ Hz, 4H), 7.45 (t, $J = 7.2$ Hz, 2H), 6.54 (d, $J = 8.9$ Hz, 1H), 6.39 (s, 1H).

2-{2-hydroxy-4-[(octyloxycarbonyl)ethylideneoxy]phenyl}-4,6-Bis(4-biphenylyl)-1,3,5-triazine (CGL-479). Stirred acetone (100 mL) in a 250 mL four-necked flask was added to intermediate 1 (4.93 g, 10.0 mmol) and K_2CO_3 (2.07 g, 15.0 mmol); the mixture was stirred for 0.5 h at 40 °C. Octyl 2-bromopropionate (2.92 g, 11.0 mmol) in 20 mL acetone was added slowly into the mixture with stirring. The reaction mixture was stirred for 6 h under reflux. The solvent was evaporated under reduced pressure, and water (50 mL) was added then extracted with CH_2Cl_2 (50 mL × 2). The organic phases were combined, dried with anhydrous $MgSO_4$, and concentrated. The residue was purified by silica gel column (DCM/Petroleum = 1:1, Rf = 0.4) to give CGL-479 (6.48 g, 9.61 mmol) as a yellow solid in a yield of 96.1%.

Melting point: 128.1 ~ 130.2 °C. IR (KBr) 3320, 3056, 2952, 2850, 1730, 1631, 1589, 1508, 1446, 1412, 1354, 1280, 1252, 1188, 1108, 946, 836, 742, 694. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ (ppm): 13.33 (s, 1H), 8.57 (dd, *J* = 19.4, 8.6 Hz, 4H), 7.93 (d, *J* = 8.3 Hz, 4H), 7.79 (d, *J* = 7.4 Hz, 4H), 7.54 (t, *J* = 7.5 Hz, 4H), 7.46 (t, *J* = 7.3 Hz, 2H), 6.63 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.44 (d, *J* = 2.3 Hz, 1H), 5.08 (q, *J* = 6.6 Hz, 1H), 4.10 (t, *J* = 7.5 Hz, 2H), 1.55–1.52 (m, 5H), 1.30–1.25 (m, 5H), 0.87–0.83 (m, 2H), 0.67 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.75, 170.95, 164.17, 163.25, 145.42, 140.05, 131.54, 129.37, 128.96, 128.13, 127.24, 111.53, 107.99, 102.48, 72.48, 65.63, 31.83, 29.23, 28.62, 25.85, 22.69, 18.53, 14.11. HRMS (ESI) m/z: calcd. for $C_{44}H_{43}N_3O_4$ 676.3175 (negative ion), found 676.3180 (negative ion).

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