Supporting Information for

A novel glycopolymeric ultraviolet absorber covering UV-A and UV-B ranges

Yanfeng Tang[a], Pengfei Gao[a], Miao Wang[a], Jinli Zhu[a]*, Xiangjian Wan[b]

[a]School of Chemistry and Chemical Engineering, Nantong University, Nantong 226019, PR China, jinlizhu@ntu.edu.cn
[b]School of Chemistry, Nankai University, Tianjing, 300071, PR China

Materials. All the chemicals including UV-0, p-hydroxy-cinnamic acid(PHC), triethylamine，acryloyl chloride (AC), 1,2,5,6-di-O-isopropylidene-α-D-glucose (DIG) and trifluoroacetic acid(TFA) are A. R. grade.

Measurements

The UV-Vis spectroscopies were measured by Shimadzu UV-720 spectrophotometer using absolute ethyl alcohol as solvent. FT-IR spectra were performed on a Nicolet Avatar 370 Fourier transform spectrometer at room temperature using the KBr pellet technique. ^{1}H NMR spectra were recorded on a Varian INOVA-400 spectrometer of 400 MHz. The ESI-MS data were tested by micrOTOF-QⅡ mass spectrometer. The molecular weights and disributions of copolymers were measured by GPC (Model 410; Waters).

Synthesis of HAB, AMC and OAIG

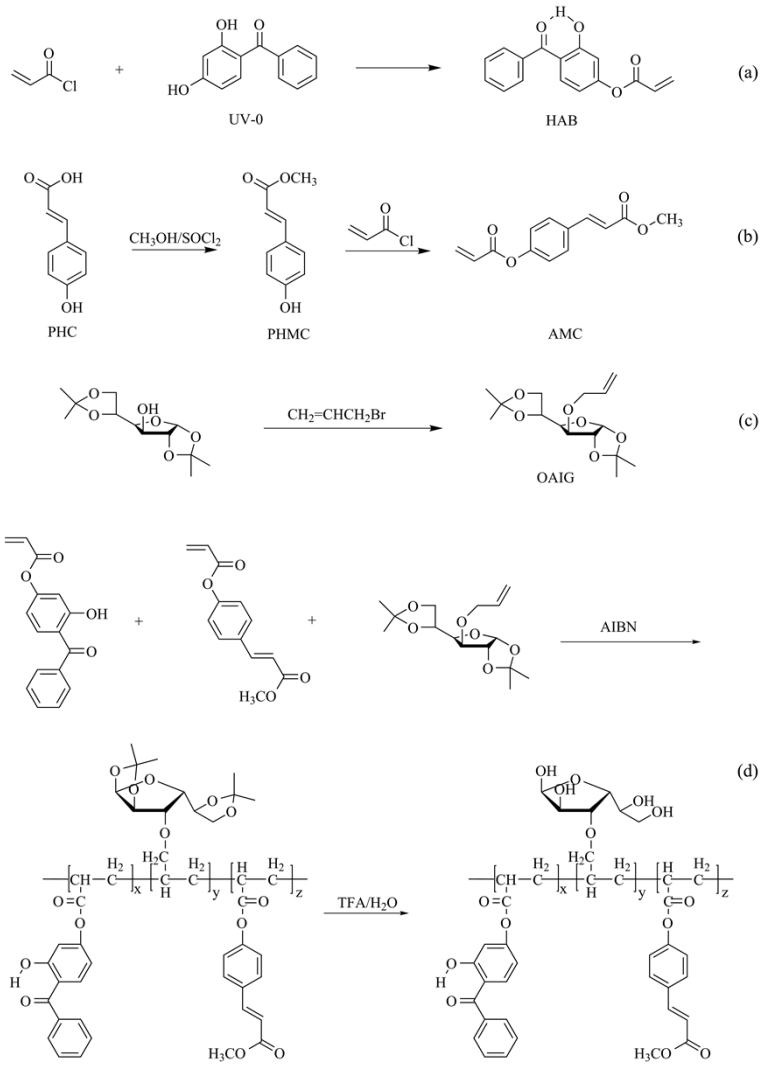
HAB was prepared similar to the procedures in a reference (Scheme 1a). A mixture of UV-0 (4.32 g, 20 mmol), triethylamine (4.3 mL, 32 mmol) and THF (15 mL) was added into a 100 mL flask. After dissolution, the reaction mixture was cooled in an ice bath. AC (2.90 g, 32 mmol) in THF (10 mL) was added to the flask. When the reaction was finished, the reaction mixture was filtered. The solution was evaporated to give a crude product. HAB was recrystallized from ethanol to yield 4.2 g (80%) as alight yellow crystal. ESI-MS: m/z=269.00[M+H]+. ^{1}H NMR (400MHz, $CDCl_3$, δ ppm): 12.27 (s, 1H); 7.67 (dd, J=9.2, 2.0 Hz, 2H); 7.65 (d, J=4.0 Hz, 1H); 7.58 (dd, J=10.2, 2.0 Hz, 1H); 7.50 (m, 2H); 6.88 (d, J=4.0 Hz, 1H); 6.69 (dd, J=11.6, 2.4 Hz, 1H); 6.63 (dd, J=24.0, 1.6 Hz, 1H); 6.31 (dd, J=24.0, 14.0 Hz, 1H); 6.06 (dd, J=14.0, 1.6 Hz, 1H). FT-IR (KBr, cm^{-1}): 3080 (C=C-H); 1740 (C=O), 1600, 1580 (phenyl ring); 1250 (C-O-C=O).

AMC was synthesized through two steps (Scheme 1b). At first, PHMC was synthesized from PHC and methanol in the presence of thionyl chloride. The second step was same to the synthesis of HAB and gave AMC 5.03 yield (85%) as a white crystal. ESI-MS: m/z=233.01[M+H]+. ^{1}H NMR (400MHz, $CDCl_3$, δ ppm): 7.69 (d, J=21.4 Hz, 1H); 7.56 (d, J=11.6 Hz, 2H); 7.18 (d, J=11.6 Hz, 2H); 6.63 (dd, J=24.0, 1.6 Hz, 1H); 6.41 (d, J=21.4 Hz, 1H); 6.32 (dd, J=24.0, 14.0 Hz, 1H); 6.04 (dd, J=14.0, 1.6 Hz, 1H); 3.81 (s, 3H). FT-IR (KBr, cm^{-1}): 3078 (C=C-H); 1735, 1710 (C=O, C=O), 1591, 1553 (phenyl ring); 1170 (C-O-C=O)

OAIG was prepared as follows. Sodium hydride (1.92 g, 80 mmol) in dry THF (30 mL) was placed in a three-necked flask. The system was filled with dry nitrogen gas and cooled to 0 ^{o}C. Then, a solution of 1,2,5,6-di-O-isopropylidene-α-D-glucose (14.06 g, 54 mmol) in anhydrous THF (60 mL) was added dropwise to the suspension with stirring. After hydrogen gas evolution finished, the cooling bath was removed and the reaction was allowed to warm up to room temperature. Then n-Bu_4NI (0.71 g) and allay bromide (10.20 g, 84.31 mmol) were added to the above mixture and stirred for 16 h. Then, a saturated aqueous solution of sodium bicarbonate was added and the mixture was extracted for three times with ether. After that, the ether extract was washed with brine, and dried with anhydrous sodium sulfate. After evaporating the solvent, the resulting pale yellow oil was distilled under reduced pressure to give OAIG (15.07 g, 50.18 mmol). ^{1}H NMR (400MHz, $CDCl_3$, δ ppm): 5.90-6.01(m, 1H); 5.77 (m, 1H); 5.24-5.38 (m, 2H); 4.65 (m, 1H); 4.20-4.30 (m, 1H); 4.02-4.11 (m, 3H); 3.68-3.95 (m, 3H); 1.60 (s, 6H), 1.35 (3, 6H). FI-IR (KBr, cm^{-1}): 3080 (C=C-H); 2986 (C-H); 1647 (C=C); 1373, 1372 (C-$(CH_3)_2$); 1216 (C-O-C).

Preparation of PHOA

A 150 mL four necked round-bottom flask with a stirrer was placed in the oil bath. After heated to 65 ºC, HAB (2.144 g, 8 mmol), AMC (0.232 g, 1 mmol) and OAIG (1.2 g, 4 mmol) in THF (50 mL), and AIBN (0.007 g) in THF (5 mL) were added in a dropwise manner to the flask, respectively. The reaction mixture was allowed to maintain at 65 ^{o}C for 24h under the protection of nitrogen. When the reaction was finished, the reaction mixture was coagulated with petroleum ether for twice, dried at 50 ^{o}C and pulverized to get PHIA. Next, the mixture of TFA and H_2O (1:1.5 mL) was added dropwise to a stirred solution of PHIA in dry THF. The reaction mixture was stirred for 1 h at room temperature. The solution was evaporated and dried in vacuo to get PHOA with a total yield 4.544 g (80%).



Scheme 1. Synthesis of HAB(a), AMC(b), OAIG(c) and PHOA(d)

Measurement of photo-antioxidant ability

Photo-antioxidant abilities were measured using an air-tight reaction system. After styrene (substrate), AIBN (photo-initiator) and the ultraviolet absorber were dissolved in ethanol (5 mL) under O_2, the autoxidation was carried out at 50 ^{o}C under ultraviolet light. Photo-antioxidant ability is reported as a relative oxidation rate (ROR), namely, a rate of oxidation velocities in the presence or absence of the ultraviolet absorber. The equation is shown below:

$$\text{Relative oxidation rate}\,\% = \frac{\text{velocity in the presence of the ultraviolet absorber}}{\text{velocity in the absence of the ultraviolet absorber}} \times 100\%$$

That is to say, the lower ROR (%) is, the higher the photo-antioxidant ability.

Measurement of biocompatibility

The cytotoxicity of PHOA was evaluated by 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay using well-grown passage L929 mouse

broblasts under the standard ISO 10993.5-1999. L929 cells were seeded in 96-well plates at a density of 1×10^4 cells per well and incubated in a humidified incubator (37 °C, 5% CO_2) for 12 h. Then the cells were treated with different concentrations of sterilize-prepared PHOA (5.0, 10.0, 15.0, and 20.0 wt.%). Copolymer-free wells cultured under the same conditions were used as controls. After 24 h treatments, 20 μL MTT solution (5 mg/mL) was added to each well and incubated for 4 h in a humidified incubator (37 °C, 5 % CO_2) to form formazan crystals. Then the culture medium was removed, and 150 μL DMSO was added to each well to solubilize formazan dye. After 15 min, the absorbance was measured at 490 nm in a microplate reader.