

Photoinitiation Properties of Heterocyclic Hexaarylbiimidazoles with High UV-Vis Absorbance

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ABSTRACT: Four heterocyclic hexaarylbiimidazoles, BFuTM-HABI, BThTM-HABI, BCTFu-HABI, and BCTTh-HABI, were synthesized to improve the UV-vis absorption properties of hexaarylbiimidazoles. UV-vis spectra, fluorescence spectra, ESR measurements, photo-dilatometer experiments, and photo-DSC measurements indicate that BCTFu-HABI and BCTTh-HABI exhibit better UV-vis absorption

abilities and photoinitiation activities for acrylate derivatives with different functionalities than BFuTM-HABI and BThTM-HABI, respectively. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2027–2035, 2007

Key words: photoinitiation; heterocyclic; hexaarylbiimidazole; acrylate derivatives

INTRODUCTION

Hexaarylbiimidazole (HABI or Lophine dimer, L₂) and its derivatives have been widely used as free radical initiators in photopolymer imaging, photoresists, etc.^{1,2} The application of HABI is based on well-established properties of its UV-photolytic dissociation.

Under UV irradiation, the homolysis of HABI derivatives at singlet state produces long-lived 2,4,5-triarylimidazolyl radicals (lophyl radicals, L•) because of the low C–N bond energy.³ The triarylimidazolyl radicals can abstract hydrogen atoms from hydrogen-donor coinitiators and consequently initiate efficient photopolymerizations of acrylate monomers.^{4,5}



There is a substantial industrial interest in developing new photopolymerizable composites containing HABI derivatives. However, the absorption bands of HABI industrially utilized lie in UV region with maximum absorption peaks below 300 nm. Moreover, their extinction coefficients at 365 nm, irradiation wavelength most widely utilized for photocuring, are unsatisfying. Therefore, it is necessary to improve the

absorption of HABI in UV-vis region around 365 nm. This article introduces some electron-rich heterocyclic groups, such as furan and thiophene groups, into HABIs' structures to enhance their UV-vis absorption abilities and photoinitiation activities.^{5–7}

EXPERIMENTAL

Materials

3,3'-Dimethoxyl benzil was obtained from Shanghai Sanshi Science and Technology Co. (Shanghai, China). Vitamin B₁ (thiamine hydrochlorate) and 2-furaldehyde were provided by China National Pharmaceutical Group Corp. (Shanghai, China). 2-Thiophenecarboxaldehyde was obtained from Zhejiang Huangyan Renmin Plant (Huangyan, China). 2-Chlorobenzaldehyde was purchased from Fluka Chemical Co. (UK). 2-Mercaptobenzoxazole (MBO) and 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) were obtained from J and K Chemical Co. (Shanghai, China). Methyl methacrylate (MMA), obtained from China National Pharmaceutical Group Corp. (Shanghai, China), was washed with 5 wt % sodium hydroxide aqueous solution and dried with calcium chloride. Poly(propylene glycol) diacrylate (PPGDA, $M_n = 540$) was provided by Aldrich Chemical Company. Trimethylolpropane triacrylate (TMPTA) was purchased from Nantong Litian Chemical Company (Nantong, China). Acrylate copolymer ($M_n = 94,000$, 40% solid content) was synthesized in our laboratory. Other chemicals were obtained from China National Pharmaceutical Group Corp. (Shanghai, China). All the reagents were used as received, exceptions were noted.

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Preparation of heterocyclic hexaarylbiimidazoles

The four heterocyclic hexaarylbiimidazoles, BFuTM-HABI, BThTM-HABI, BCTFu-HABI, and BCTTh-HABI were prepared according to the general synthesis process of hexaarylbiimidazoles (Scheme 1).^{1,8,9} As discussed earlier by Cohen, etc., the N₁-C₂ dimer structure of hexaarylbiimidazoles (shown above in Scheme 1) is widely accepted as the most stable isomer.⁷

Representative detailed experimental procedures for each heterocyclic hexaarylbiimidazole and its intermediates are provided below.

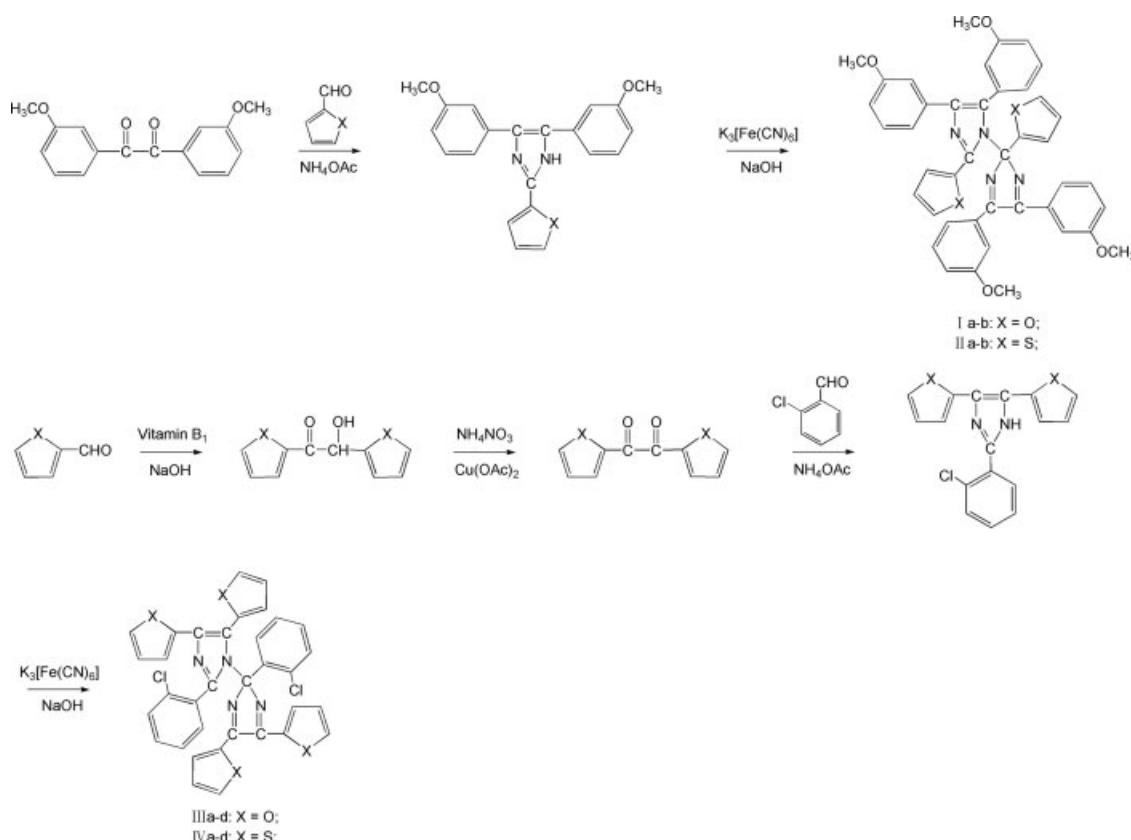
2-(2-furan)-4,5-bi-(3-methoxyphenyl)-imidazole (Ia)

A mixture of 3,3'-dimethoxy benzil (5.0 g, 18.50 mmol), acetic acid (15.0 mL), ammonium acetate (7.2 g, 92.50 mmol), and 2-furaldehyde (1.86 mL, 22.20 mmol) was refluxed for 12 h under nitrogen. The cooled mixture was then poured into 1.0 wt % sodium bisulfite aqueous solution to deplete excess aldehyde. The yellow precipitate was isolated by suction filtration, washed with water, and dried in a vacuum oven overnight. 6.20 g, 97% yield; m.p.: 224~225°C; ¹H NMR (DMSO-d₆, δ, ppm): 12.83 (s, 1H, N-H), 7.81 (m, 1H, adjacent to the oxygen atoms of furans), 7.30–6.92 (m, 8H, aromatic), 6.80–6.64 (m,

2H, furans), 3.86–3.66 (s, 6H, 2-OCH₃); FTIR (KBr disc, cm⁻¹): 3650–3250 (m, ν_{N-H}), 3140 (m, ν_{C-H} of furan), 2940 (m, ν_{O-CH₃}), 1600 (s, ν_{C=C}), 1500–1460 (m, ν_{C=C} of phenyls), 1430 (m, δ_{O-CH₃}), 1235 (s, ν_{as C-O-C} of -OCH₃), 1050 (m, ν_{s C-O-C} of -OCH₃), 785–740 (m, δ_{C-H} of phenyls).

2,2'-bis(2-furan)-4,4',5,5'-tetra-(3-methoxyphenyl)-1,2'-biimidazole (BFuTM-HABI, Ib)

In a three-necked flask, the mixture of potassium ferricyanide (8.60 g, 26.00 mmol), sodium hydroxide (3.46 g, 86.60 mmol), and water (10.0 mL) was stirred at room temperature. The solution of Ia (3.0 g, 8.66 mmol) in dichloromethane (15.0 mL) was added drop wise. The mixture was refluxed at 40°C for 12 h. After cooling, the mixture was extracted with 3 × 40 mL dichloromethane. The dichloromethane layer was washed with 100 mL of water and dried with anhydrous sodium sulfate. The dichloromethane layer was distilled partly and poured into 10-fold petroleum ether to give a yellow powder, which was recrystallized in a solution of ethanol and water. 1.87 g, 63% yield; m.p.: 184~186°C; MALDI-TOF-MS: *m/z* 691 (M+H)⁺; ¹H NMR (DMSO-d₆, δ, ppm): 7.83 (m, 2H, adjacent to the oxygen atoms of furans) 7.50–6.90 (m, 16H, aromatic), 6.74–6.56 (m, 4H, furans), 3.90–3.64 (s, 12H, 4-OCH₃); FTIR (KBr disc, cm⁻¹): 3130 (m, ν_{C-H}



Scheme 1 Synthesis of heterocyclic HABIs.

of furan), 2940 (m, $\nu_{\text{O}-\text{CH}_3}$), 1600 (s, $\nu_{\text{C}=\text{C}}$), 1500–1460 (m, $\nu_{\text{C}=\text{C}}$ of phenyls), 1430 (m, $\delta_{\text{O}-\text{CH}_3}$), 1290 (s, $\nu_{\text{as C}-\text{O}-\text{C}}$ of $-\text{OCH}_3$), 1040 (m, $\nu_{\text{s C}-\text{O}-\text{C}}$ of $-\text{OCH}_3$), 785–740 (m, $\delta_{\text{C}-\text{H}}$ of phenyls); Elemental analysis for $\text{C}_{42}\text{H}_{34}\text{N}_4\text{O}_6$: C, 73.24% (73.03%, calcd.), H, 4.96% (4.96%), N, 7.56% (8.11%).

2-(2-thiophene)-4,5-bi-(3-methoxyphenyl)-imidazole (IIa)

A mixture of 3,3'-dimethoxy benzil (5.0 g, 18.50 mmol), acetic acid (15.0 mL), ammonium acetate (7.2 g, 92.50 mmol), and 2-thiocarboxaldehyde (2.10 mL, 22.20 mmol) was refluxed for 12 h under nitrogen. The cooled mixture was then poured into 1.0 wt % sodium bisulfite aqueous solution. The yellow precipitate was isolated by suction filtration, washed with water, and dried in a vacuum oven. 6.17 g, 92% yield; m.p.: 188~189°C; ^1H NMR (DMSO- d_6 , δ , ppm): 12.77 (s, 1H, N-H), 7.70 (m, 1H, adjacent to the sulfur atoms of thiophenes), 7.54–7.05 (m, 8H, aromatic), 6.95–6.78 (m, 2H, thiophenes), 3.73–3.66 (s, 6H, 2- OCH_3); FTIR (KBr disc, cm^{-1}): 3650–3300 (m, $\nu_{\text{N}-\text{H}}$), 3075 (m, $\nu_{\text{C}-\text{H}}$ of thiophene), 2950 (m, $\nu_{\text{O}-\text{CH}_3}$), 1600 (s, $\nu_{\text{C}=\text{C}}$), 1500–1460 (m, $\nu_{\text{C}=\text{C}}$ of phenyls), 1430 (m, $\delta_{\text{O}-\text{CH}_3}$), 1230 (s, $\nu_{\text{as C}-\text{O}-\text{C}}$ of $-\text{OCH}_3$), 1050 (m, $\nu_{\text{s C}-\text{O}-\text{C}}$ of $-\text{OCH}_3$), 785–740 (m, $\delta_{\text{C}-\text{H}}$ of phenyls).

2,2'-bis(2-thiophene)-4,4',5,5'-tetra-(3-methoxyphenyl)-1,2'-biimidazole (BTHM-HABI, IIb)

In a three-necked flask, the solution of potassium ferriocyanide (8.20 g, 24.90 mmol), sodium hydroxide (3.32 g, 82.80 mmol), and water (10.0 mL) was stirred at room temperature. The mixture of IIa (3.0 g, 8.28 mmol) in dichloromethane (15.0 mL) was added drop wise. The mixture was refluxed at 40°C for 12 h. After cooling, the mixture was extracted with 3 \times 40 mL dichloromethane. The dichloromethane layer was washed with 100 mL of water and dried with anhydrous sodium sulfate. The dichloromethane layer was distilled partly and poured into 10-fold petroleum ether to give a yellow powder, which was recrystallized in a solution of ethanol and water. 2.66 g, 89% yield; m.p.: 128~130°C; MALDI-TOF-MS: m/z 723 ($\text{M}+\text{H}^+$); ^1H NMR (DMSO- d_6 , δ , ppm): 7.95 (m, 2H, adjacent to the sulfur atoms of thiophenes), 7.48–7.00 (m, 16H, aromatic), 6.80–6.65 (m, 4H, thiophenes), 3.76–3.63 (s, 12H, 4- OCH_3); FTIR (KBr disc, cm^{-1}): 3075 (m, $\nu_{\text{C}-\text{H}}$ of thiophene), 2950 (m, $\nu_{\text{O}-\text{CH}_3}$), 1600 (s, $\nu_{\text{C}=\text{C}}$), 1500–1460 (m, $\nu_{\text{C}=\text{C}}$ of phenyls), 1430 (m, $\delta_{\text{O}-\text{CH}_3}$), 1230 (s, $\nu_{\text{as C}-\text{O}-\text{C}}$ of $-\text{OCH}_3$), 1050 (m, $\nu_{\text{s C}-\text{O}-\text{C}}$ of $-\text{OCH}_3$), 785–740 (m, $\delta_{\text{C}-\text{H}}$ of phenyls); Elemental analysis for $\text{C}_{42}\text{H}_{34}\text{N}_4\text{O}_4\text{S}_2$: C, 68.03% (69.78%, calcd.), H, 4.91% (4.74%), N, 7.37% (7.75%).

Furoin (IIIa)

A 150 mL three-necked flask was charged with vitamin B₁ (3.50 g, 0.01 mol), water (7.0 mL), and 95 wt % ethanol (30.0 mL). Sodium hydroxide (10 wt %) aqueous solution was added dropwise under nitrogen at 0°C. 2-Furaldehyde (16.7 mL, 0.20 mol) was then added dropwise at room temperature. The resulting solution was refluxed under nitrogen for 6 h. After cooling, the white crystals were filtered, washed, and dried. The crude crystals were recrystallized from ethanol to give white needle-like crystals. 16.5 g, 86% yield; m.p.: 135~136°C (134~138°C, lit.); ^1H NMR (DMSO- d_6 , δ , ppm): 8.00 (m, 2H, adjacent to oxygen atoms of furans), 7.45–6.90 (m, 4H, furans), 6.60–6.45 (w, 1H, $-\text{OH}$), 6.05 (m, 1H, $>\text{CH}-$); FTIR (KBr disc, cm^{-1}): 3650–3160 (m, $\nu_{\text{O}-\text{H}}$), 3125 (m, $\nu_{\text{C}-\text{H}}$ of furan), 1680 (s, $\nu_{\text{C}=\text{O}}$), 1550 (w, $\nu_{\text{C}=\text{C}}$ of furan), 1460 (m, $\delta_{\text{O}-\text{H}}$), 1250 and 1210 (m, $\nu_{\text{C}-\text{O}}$).

Furil (IIIb)

A solution of cupric acetate (0.12 g, 0.58 mmol), ammonium nitrate (5.90 g, 73.85 mmol), acetic acid (10.0 mL), and water (5.0 mL) were heated to 80°C. A mixture of IIIa (10.0 g, 52.04 mmol) and acetic acid (30.0 mL) was added drop wise. The resulting mixture was refluxed at 110°C for 12 h. The solution was cooled slowly to room temperature followed by cooling to 5~10°C. The yellow crystal was filtered, washed, and dried in a vacuum oven. 7.70 g, 78% yield; m.p.: 167~168°C (163~165°C, lit.); ^1H NMR (DMSO- d_6 , δ , ppm): 8.25 (m, 2H, adjacent to oxygen atoms of furans), 8.00 (m, 2H, adjacent to acyls), 7.30 (m, 2H, meta-posed to oxygen atoms of furans); FTIR (KBr disc, cm^{-1}): 3150 (m, $\nu_{\text{C}-\text{H}}$ of furan), 1650 (s, $\nu_{\text{C}=\text{O}}$), 1550 (w, $\nu_{\text{C}=\text{C}}$ of furan).

2-(2-chlorophenyl)-4,5-bi-(2-furan)-imidazole (IIIc)

A mixture of IIIb (5.0 g, 26.30 mmol), acetic acid (15.0 mL), ammonium acetate (10.2 g, 0.13 mol), and 2-chlorobenzaldehyde (3.30 mL, 31.56 mmol) was refluxed for 12 h under nitrogen. After cooling, the solution was poured into 1.0 wt % sodium bisulfite aqueous solution. The yellow precipitate was isolated by suction filtration, washed with water, and dried in a vacuum oven. 7.45 g, 91% yield; m.p.: 245~246°C; ^1H NMR (DMSO- d_6 , δ , ppm): 12.83 (s, 1H, N-H), 7.81 (m, 2H, adjacent to the oxygen atom of furan), 7.30–6.92 (m, 4H, aromatic), 6.80–6.64 (m, 4H, furans); FTIR (KBr disc, cm^{-1}): 3650–3260 (m, $\nu_{\text{N}-\text{H}}$), 3060 (m, $\nu_{\text{C}-\text{H}}$ of furan), 2930 (w, $\nu_{\text{C}-\text{H}}$ of phenyl), 1640 (s, $\nu_{\text{C}=\text{C}}$), 1600, 1480, and 1300 (m, $\nu_{\text{C}=\text{C}}$ of furan), 1540 and 1450 (m, $\nu_{\text{C}=\text{C}}$ of phenyl), 1050 (m, $\nu_{\text{C}-\text{Cl}}$), 1020 (m, $\nu_{\text{C}-\text{O}-\text{C}}$), 880 and 740 (m, $\delta_{\text{C}-\text{H}}$ of furan).

2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetra-(2-furan)-1,2'-biimidazole (BCTFu-HABI, IIIId)

In a three-necked flask were placed potassium ferricyanide (15.9 g, 48.30 mmol), sodium hydroxide (6.5 g, 0.16 mol), and water (15.0 mL). The solution of IIIc (5.0 g, 16.10 mmol) in dichloromethane (25.0 mL) was added drop wise. The resulting mixture was refluxed at 40°C for 12 h. The mixture was extracted with 3 × 50 mL dichloromethane. The organic phase was dried over anhydrous sodium sulfate and concentrated. The organic phase was then poured into 10-fold petroleum ether. The precipitate was recrystallized from a solution of ethanol and water to give a pale-yellow crystal. 3.56 g, 71% yield; m.p.: 198~199°C; MALDI-TOF-MS: m/z 620 (M+H)⁺; ¹H NMR (DMSO-d₆, δ, ppm): 7.83 (m, 4H, adjacent to the oxygen atom of furans), 7.50–6.90 (m, 8H, aromatic), 6.74–6.56 (m, 8H, furans); FTIR (KBr disc, cm⁻¹): 3060 (w, ν_{C-H} of furan), 2960, 2935, and 2875 (m, ν_{CH} of phenyl), 1620 (s, ν_{C=C}), 1570, 1470, and 1300 (m, ν_{C=C} of furan), 1520 and 1380 (m, ν_{C=C} of phenyl), 1060 (m, ν_{C-Cl}), 1030 (m, ν_{C-O-C}), 880 and 750 (m, δ_{C-H} of furan); Elemental analysis for C₃₄H₂₀N₄O₄Cl₂: C, 65.79% (65.92%, calcd.), H, 3.49%(3.25%), N, 8.96%(9.04%).

Thiophene acyloin (IVa)

A 150 mL three-necked flask was charged with vitamin B₁ (3.50 g, 0.01 mol), water (7.0 mL) and 95 wt % ethanol (30.0 mL). Sodium hydroxide (10 wt %) aqueous solution was added drop wise under nitrogen at 0°C. After this, 2-thiophenecarboxaldehyde (18.7 mL, 0.20 mol) was added drop wise at room temperature. The resulting solution was refluxed under nitrogen for 6 h. After cooling, the white crystals were filtered, washed, and dried. The crude crystals were recrystallized from ethanol to give white needle-like crystals. 18.0 g, 80% yield; m.p.: 104~105°C; ¹H NMR (DMSO-d₆, δ, ppm): 8.25–8.00 (m, 2H, adjacent to sulfur atoms of thiophenes), 7.45–6.93 (m, 4H, thiophenes), 6.60–6.45 (w, 1H, –OH), 6.08 (m, 1H, >CH–); FTIR (KBr disc, cm⁻¹): 3550–3130 (m, ν_{O-H}), 3120 (m, ν_{C-H} of thiophene), 1650 (s, ν_{C=O}), 1515 (w, ν_{C=C} of thiophene), 1410 (m, δ_{O-H}), 1240 and 1200 (m, ν_{C-O}).

Thiophene diacyl (IVb)

A solution of cupric acetate (0.12 g, 0.58 mmol), ammonium nitrate (5.90 g, 73.85 mmol), acetic acid (10.0 mL), and water (5.0 mL) was heated to 80°C. A mixture of IVa (10.0 g, 44.60 mmol) and acetic acid (30.0 mL) was added dropwise. The resulting mixture was refluxed at 110°C for 12 h. The solution was cooled slowly to room temperature followed by chilling to 5~10°C. The yellow crystal was filtered, washed, and

dried in a vacuum oven. 8.50 g, 86% yield; m.p.: 82~83°C; ¹H NMR (DMSO-d₆, δ, ppm): 8.27 (m, 2H, adjacent to sulfur atoms of thiophenes), 8.01 (m, 2H, adjacent to acyls), 7.31 (m, 2H, meta-posed to sulfur atoms of thiophenes); FTIR (KBr disc, cm⁻¹): 3100 (m, ν_{C-H} of thiophene), 1640 (s, ν_{C=O}), 1500 (w, ν_{C=C} of thiophene).

2-(2-chlorophenyl)-4,5-bi-(2-thiophene)-imidazole (IVc)

A mixture of IVb (5.0 g, 22.50 mmol), acetic acid (15.0 mL), ammonium acetate (8.5 g, 0.11 mol), and 2-chlorobenzaldehyde (2.80 mL, 27.00 mmol) was refluxed for 12 h under nitrogen. After cooling, the solution was poured into 1.0 wt % sodium bisulfite aqueous solution. The yellow precipitate was isolated by suction filtration, washed with water, and dried in a vacuum oven. 7.18 g, 93% yield; m.p.: 221~222°C; ¹H NMR (DMSO-d₆, δ, ppm): 12.80 (s, 1H, N–H), 8.10–7.80 (m, 2H, adjacent to the sulfur atoms of thiophenes), 7.80–7.25 (m, 4H, aromatic), 7.25–6.55 (m, 4H, thiophenes); FTIR (KBr disc, cm⁻¹): 3650–3250 (m, ν_{N-H}), 3090 (w, ν_{C-H} of thiophene), 2960, 2930 and 2860 (w, ν_{CH} of phenyl), 1600 (s, ν_{C=C} of imidazole), 1560 and 1470 (m, ν_{C=C} of phenyl), 1500, 1420, and 1300 (m, ν_{C=C} of thiophene), 1085 (m, ν_{C-Cl}), 845 and 750 (m, δ_{C-H} of thiophene).

2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetra-(2-thiophene)-1,2'-biimidazole (BCTTh-HABI, IVd)

In a three-necked flask were placed potassium ferricyanide (15.9 g, 48.30 mmol), sodium hydroxide (6.5 g, 0.16 mol), and water (15.0 mL). The solution of IVc (5.0 g, 14.60 mmol) in dichloromethane (25.0 mL) was added drop wise. The resulting mixture was refluxed at 40°C for 12 h. The mixture was extracted with 3 × 50 mL dichloromethane. The organic phase was dried over anhydrous sodium sulfate and concentrated. The organic phase was then poured into 10-fold petroleum ether. The precipitate was recrystallized from a solution of ethanol and water to give a pale-yellow crystal. 3.50 g, 70% yield; m.p.: 188~189°C; MALDI-TOF-MS: m/z 684 (M+H)⁺; ¹H NMR (DMSO-d₆, δ, ppm): 8.10–7.80 (m, 4H, adjacent to the sulfur atoms of thiophenes), 7.80–7.25 (m, 8H, aromatic), 7.25–6.55 (m, 8H, thiophenes); FTIR (KBr disc, cm⁻¹): 3090 (w, ν_{C-H} of thiophene), 2960, 2930, and 2860 (w, ν_{CH} of phenyl), 1600 (s, ν_{C=C} of imidazole), 1560 and 1470 (m, ν_{C=C} of phenyl), 1500, 1420, and 1300 (m, ν_{C=C} of thiophene), 1090 (m, ν_{C-Cl}), 845 and 750 (m, δ_{C-H} of thiophene); Elemental analysis for C₃₄H₂₀N₄S₄Cl₂: C, 60.32%(59.73%, calcd.), H, 3.09%(2.95%), N, 7.85% (8.19%).

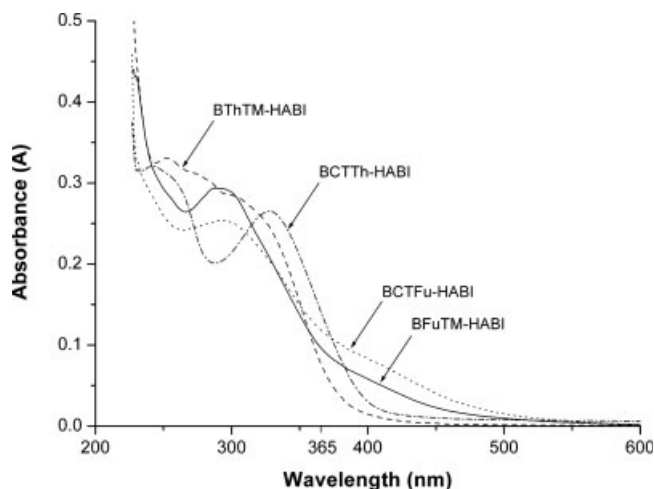


Figure 1 UV-vis absorption spectra of BFuTM-HABI, BThTM-HABI, BCTFu-HABI, and BCTTh-HABI in chloroform, with a concentration of 1.0×10^{-5} mol/L.

Instruments

Melting points (m.p.) of the four heterocyclic hexaarylbiimidazoles and their intermediates were determined with a XT-4 binocular micromelting point apparatus of Taike apparatus Co., Beijing, China.

^1H NMR spectra were recorded on a Varian Mercury Plus-400 nuclear magnetic resonance spectrometer (400 MHz). FTIR spectra were recorded on a Perkin-Elmer Paragon 1000 spectrophotometer. Mass spectra were determined on an Agilent HP1100 matrix-assisted laser desorption ionization time-of-flight mass spectrometer (MALDI-TOF-MS). Elemental analysis was carried out on an Elementar Vario EL apparatus.

UV-vis spectra were recorded on a Perkin-Elmer Lambda 20 spectrophotometer. BFuTM-HABI, BThTM-HABI, BCTFu-HABI, and BCTTh-HABI were dissolved, respectively, in chloroform with a concentration of 1.0×10^{-5} mol/L.

Fluorescence spectra were recorded on a Perkin-Elmer LS-50B spectrophotometer. BFuTM-HABI, BThTM-HABI, BCTFu-HABI, and BCTTh-HABI were dissolved separately in chloroform, with a concentration of 1.0×10^{-5} mol/L. In each solution, a coinitiator MBO was added with a concentration of 1.0×10^{-5} mol/L.

ESR spectra were recorded on a Bruker EMX-8 EPR spectrometer at 9.78 GHz with a modulation frequency of 100 KHz and DMPO was used as a radical-capturing agent. A Bruker Lanyze HBO 50 W high pressure mercury lamp was used for the irradiation at 25°C in the ESR spectrometer cavity. BFuTM-HABI, BThTM-HABI, BCTFu-HABI, and BCTTh-HABI were dissolved respectively, in dichloromethane, with a concentration of 1.0×10^{-3} mol/L. In each solution, MBO was added with a concentration of 2.0×10^{-3}

mol/L. Sample solution (0.5 mL) was dropped into a quartz ESR tube and then degassed with nitrogen. Under the irradiation, the intensity of ESR signals is proportional to the amount of radicals captured by DMPO.

Photo-dilatometer experiments were carried out in a 12 mL dilatometer at 30°C with a 400 W high pressure mercury lamp. The distance between the axis of lamp and the dilatometer is 300 mm. Before irradiation, the solutions of photoinitiator, MBO, MMA, and DMF were degassed with nitrogen.

Photo-DSC measurements were carried out with a photo-differential scanning calorimetry 6200 (Seiko Instrument). A high pressure mercury lamp with a cut-off filter (365 nm) was used for irradiation. The solutions of 0.1516 mmol photoinitiator, 0.0458 g MBO, 2.0 g crosslinker (PPGDA or TMPTA), 5.0 g acrylate copolymer, and 1.5 g toluene were coated on PET films and dried in an oven. Approximately 2.0 mg dry films with 40 μm thickness were irradiated for 3 min on photo-DSC with a $50 \text{ mW}/\text{cm}^2$ light intensity under a 50 mL/min nitrogen flow at 25°C .

RESULTS AND DISCUSSION

Photochemical behaviors

UV-vis absorption spectra

The UV-vis absorption spectra of BFuTM-HABI, BThTM-HABI, BCTFu-HABI, and BCTTh-HABI are described as Figure 1 and Table I. According to Figure 1 and Table I, they strongly absorb UV light with the major absorption maxima at 280~330 nm. These absorption peaks are attributed to the $S_0 \rightarrow S_1$ (π , π^*) transition of biimidazole.^{4,10} The existence of electron-rich atoms O and S lead to the red-shift of absorption peaks of hexaarylbiimidazoles.⁷ Especially, thiophene groups influence remarkably the absorption peaks of biimidazoles to red-shift. BThTM-HABI absorbs strongly UV light from 240 to 330 nm, without a distinct absorption maximum. BCTTh-HABI exhibits an absorption maximum at 328 nm, much higher than that of BCTFu-HABI (293 nm). The peaks at about 240 nm of BThTM-HABI and BCTTh-HABI are attributed to the absorption of thiophene groups.

TABLE I
UV-Vis Absorption Parameters of BFuTM-HABI, BThTM-HABI, BCTFu-HABI, and BCTTh-HABI in Chloroform, with a Concentration of 1.0×10^{-5} mol/L

Comp.	λ_{max} (nm)	ϵ_{max} (L/mol/cm)	$\epsilon_{365 \text{ nm}}$ (L/mol/cm)
BFuTM-HABI	288	2.94×10^4	9.77×10^3
BThTM-HABI	301	2.84×10^4	7.94×10^3
BCTFu-HABI	293	2.54×10^4	1.19×10^4
BCTTh-HABI	328	2.65×10^4	1.44×10^4

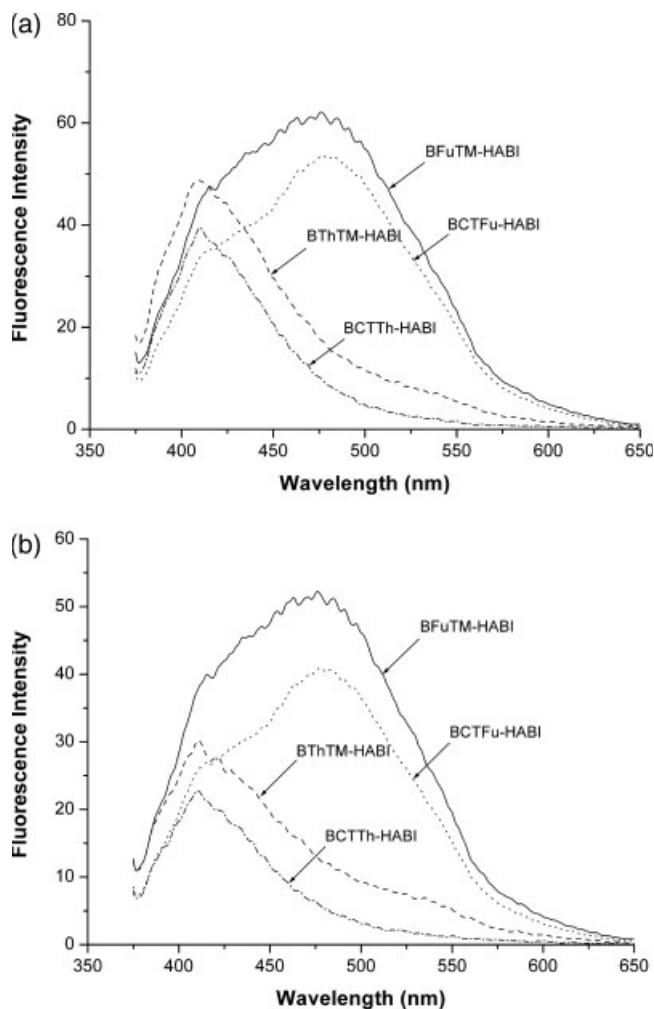


Figure 2 Fluorescence spectra of BFuTM-HABI, BThTM-HABI, BCTFu-HABI, and BCTTh-HABI without MBO (a) and with MBO (b). The concentration of BFuTM-HABI, BThTM-HABI, BCTFu-HABI, and BCTTh-HABI in chloroform is 1.0×10^{-5} mol/L and the concentration of MBO is 1.0×10^{-5} mol/L. $\lambda_{\text{exc}} = 365$ nm.

The extinction coefficient of hexaarylimidazoles at 365 nm, the major irradiation wavelength for photocuring, is one of the crucial factors to influence their photoinitiation efficiency. As shown in Figure 1, the extinction coefficient $\epsilon_{365 \text{ nm}}$ of BCTTh-HABI is higher than that of BCTFu-HABI. However, the extinction coefficient $\epsilon_{365 \text{ nm}}$ of BThTM-HABI is similar to that of BFuTM-HABI.

Fluorescence spectra

Fluorescence spectra of BFuTM-HABI, BThTM-HABI, BCTFu-HABI, and BCTTh-HABI are described as Figure 2 and Table II. Figure 2(a) shows the fluorescence spectra of them without the addition of MBO and Figure 2(b) shows the fluorescence spectra of them with the addition of MBO. As shown in Figure 2(a),

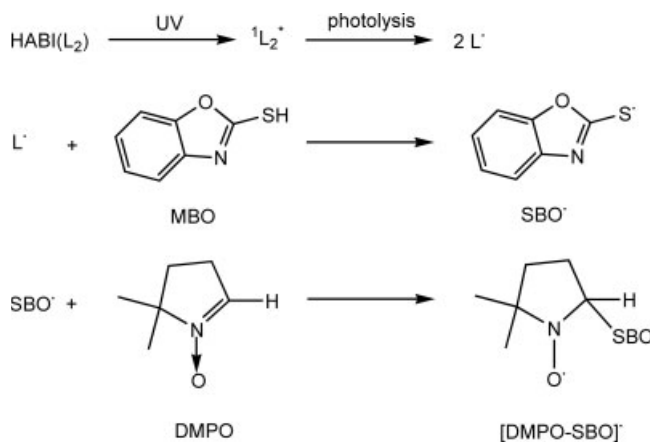
TABLE II
Fluorescence Properties of BFuTM-HABI, BThTM-HABI, BCTFu-HABI, and BCTTh-HABI in Chloroform, with a Concentration of 1.0×10^{-5} mol/L ($\lambda_{\text{exc}} = 365$ nm)

Comp.	λ_{max} (nm)	Intensity ₁ (without MBO)	Intensity ₂ (with MBO)
BFuTM-HABI	476	62.16	52.23
BThTM-HABI	410	48.70	30.15
BCTFu-HABI	477	53.56	40.77
BCTTh-HABI	410	39.55	22.75

BFuTM-HABI, BThTM-HABI, BCTFu-HABI, and BCTTh-HABI emit weak fluorescence when excited at 365 nm. The weak fluorescence is related to the quick dissociation of their excimers. Moreover, BThTM-HABI and BCTTh-HABI emit weaker fluorescence than BFuTM-HABI and BCTFu-HABI, respectively. As shown in Figure 2(b), BFuTM-HABI/MBO, BThTM-HABI/MBO, BCTFu-HABI/MBO, and BCTTh-HABI/MBO emit weaker fluorescence than BFuTM-HABI, BThTM-HABI, BCTFu-HABI, and BCTTh-HABI, respectively. This can be ascribed to the fast quenching of their excimers by MBO. This indicates the quick proton transfer between triarylimidazolyl radicals and MBO. The proton transfer process is indispensable for hexaarylimidazole/coinitiator system to initiate efficiently photopolymerizations of acrylate derivatives.¹¹

ESR measurements

ESR signals of 2-sulfurbenzoxazole radicals produced from BFuTM-HABI/MBO, BThTM-HABI/MBO, BCTFu-HABI/MBO, and BCTTh-HABI/MBO systems can be experimentally detected when DMPO is used as a radical-capturing agent (Scheme 2).¹² Spinning-trapping experiments of BFuTM-HABI/MBO, BThTM-HABI/MBO, BCTFu-HABI/MBO, and BCTTh-HABI/MBO



Scheme 2 Spinning-trapping mechanism of DMPO.

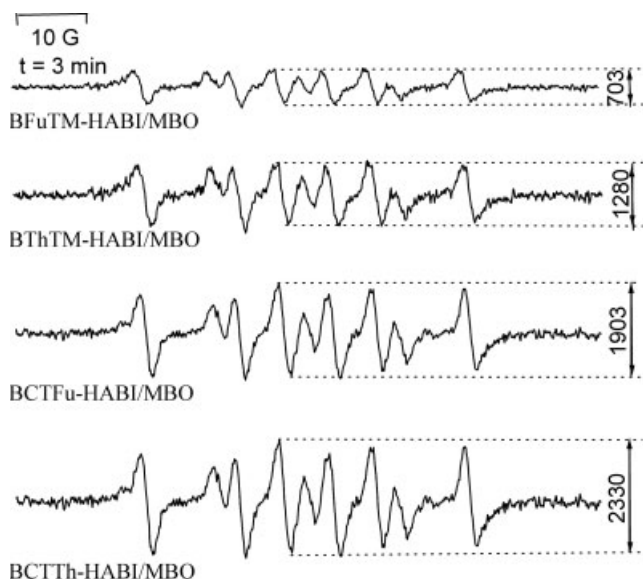


Figure 3 ESR spectra of 2-sulfurbenzoxazole radicals produced from BFuTM-HABI/MBO, BThTM-HABI/MBO, BCTFu-HABI/MBO, and BCTTh-HABI/MBO and captured by DMPO. The concentrations of BFuTM-HABI, BThTM-HABI, BCTFu-HABI, and BCTTh-HABI in dichloromethane are 1.0×10^{-3} mol/L and the concentration of MBO is 2.0×10^{-3} mol/L.

systems show similar superfine sextuple peaks (Fig. 3). The superfine sextuple peaks can be ascribed to a triple peak of α -nitrogen and its further split with β -hydrogen. The intensity of ESR signals reveals obviously the amount of 2-sulfurbenzoxazole radicals.

As shown in Figure 3, when irradiated with a 50 W high pressure mercury lamp at 25°C, BCTFu-HABI/MBO system and BCTTh-HABI/MBO system produce more 2-sulfurbenzoxazole radicals than BFuTM-HABI/MBO system and BThTM-HABI/MBO system, respectively. The smaller amounts of 2-sulfurbenzoxazole radicals in BFuTM-HABI/MBO and BThTM-HABI/MBO systems indicate that electron-rich substituents in 2-position of hexaarylbiimidazoles are disadvantageous to enhance their activities to react with hydrogen donors. This result is coincident with Cohen's work.⁷ UV-vis absorption ability of hexaarylbiimidazoles and the activity of triarylimidazolyl radicals to react with MBO influence simultaneously the amount of 2-sulfurbenzoxazole radicals. As shown in Figure 1, the extinction coefficients $\epsilon_{365 \text{ nm}}$ of BCTTh-HABI and BCTFu-HABI are higher than those of BFuTM-HABI and BThTM-HABI. Additionally, chlorine atoms contained in BCTTh-HABI and BCTFu-HABI can facilitate the radicals dissociated from them to abstract hydrogen atoms from MBO.⁷ Therefore, BCTTh-HABI/MBO and BCTFu-HABI/MBO systems produce larger amounts of 2-sulfurbenzoxazole radicals than BThTM-HABI/MBO and BFuTM-HABI/MBO systems.

Photopolymerization of MMA

The conversion of MMA is determined by the volume shrinkage of MMA in the dilatometer. Figure 4 shows the photopolymerization of MMA initiated by BFuTM-HABI/MBO, BThTM-HABI/MBO, BCTFu-HABI/MBO, and BCTTh-HABI/MBO, respectively. The photoinitiation activities of BCTFu-HABI/MBO and BCTTh-HABI/MBO are higher than those of BFuTM-HABI/MBO and BThTM-HABI/MBO, respectively. In the low-viscosity polymerization system, the amount of 2-sulfurbenzoxazole radicals affects evidently the initiation activities of HABIs. As shown in Figure 3, the amounts of 2-sulfurbenzoxazole radicals in BCTFu-HABI/MBO and BCTTh-HABI/MBO systems are much larger than those in BFuTM-HABI/MBO and BThTM-HABI/MBO systems. It leads to the higher photoinitiation activities of BCTFu-HABI/MBO and BCTTh-HABI/MBO systems consequently.

Photopolymerization of PPGDA

The reaction heat emitted in the photopolymerization is directly proportional to the number of vinyl groups reacted in the system. By detecting the exothermal process, the conversion of vinyl groups (C) and the rate of photopolymerization (R_p) can be determined.^{13–16}

Photopolymerizations of PPGDA initiated by BFuTM-HABI/MBO, BThTM-HABI/MBO, BCTFu-HABI/MBO, and BCTTh-HABI/MBO systems are described as Figure 5(a–c). Figure 5(a) indicates that

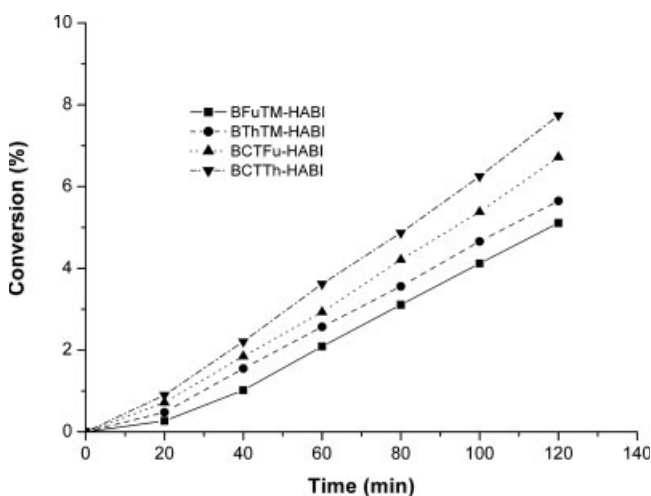


Figure 4 Conversion versus time curves of polymerization of MMA initiated by BFuTM-HABI/MBO, BThTM-HABI/MBO, BCTFu-HABI/MBO, and BCTTh-HABI/MBO systems, cured at 30°C with a 400 W high pressure mercury lamp set at a distance of 300 mm from the dilatometer. [BFuTM-HABI] = [BThTM-HABI] = [BCTFu-HABI] = [BCTTh-HABI] = 1.0×10^{-3} mol/L, [MBO] = 2.0×10^{-3} mol/L, and [MMA] = 5.0 mol/L.

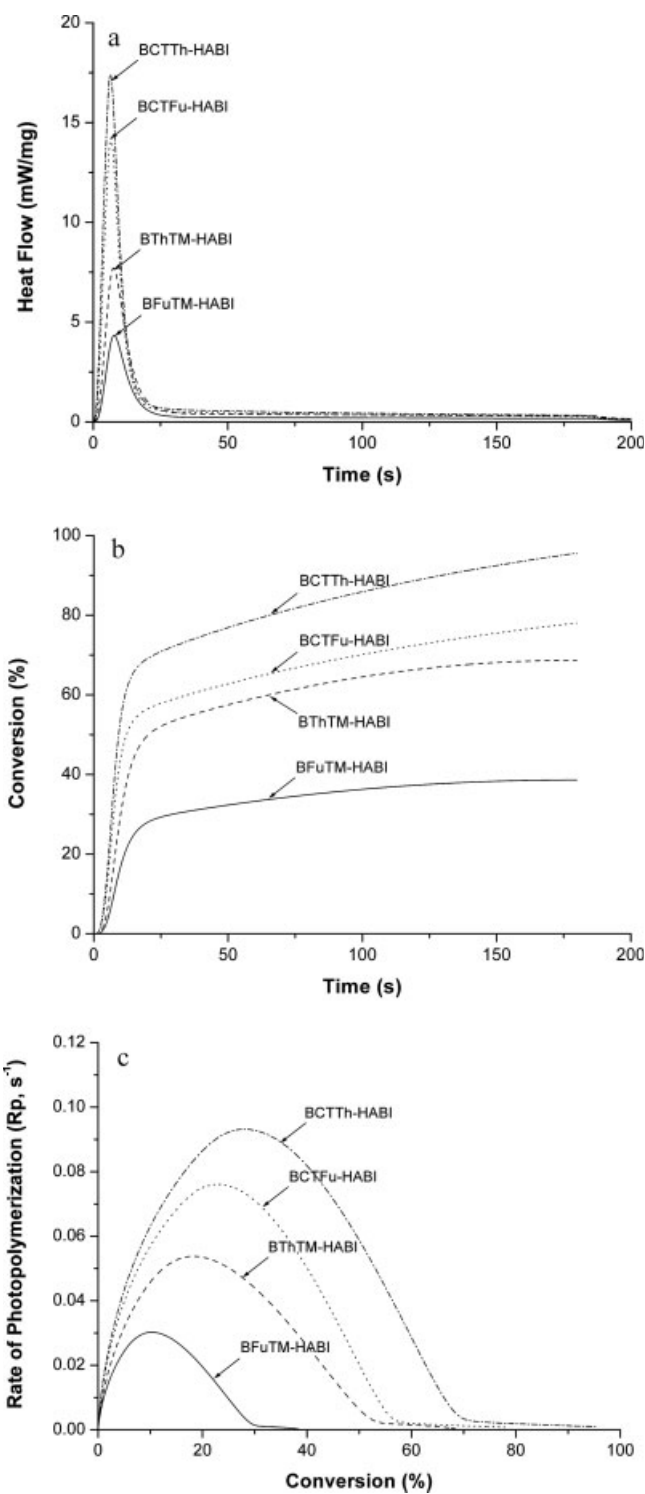


Figure 5 Heatflow versus time curves of PPGDA (a), conversion versus time curves of PPGDA (b) and R_p versus conversion curves of PPGDA, (c) initiated by BFuTM-HABI/MBO, BThTM-HABI/MBO, BCTFu-HABI/MBO, and BCTTh-HABI/MBO systems, irradiated for 3 min at 25°C with a 50 mW/cm² light intensity under a 50 mL/min nitrogen flow.

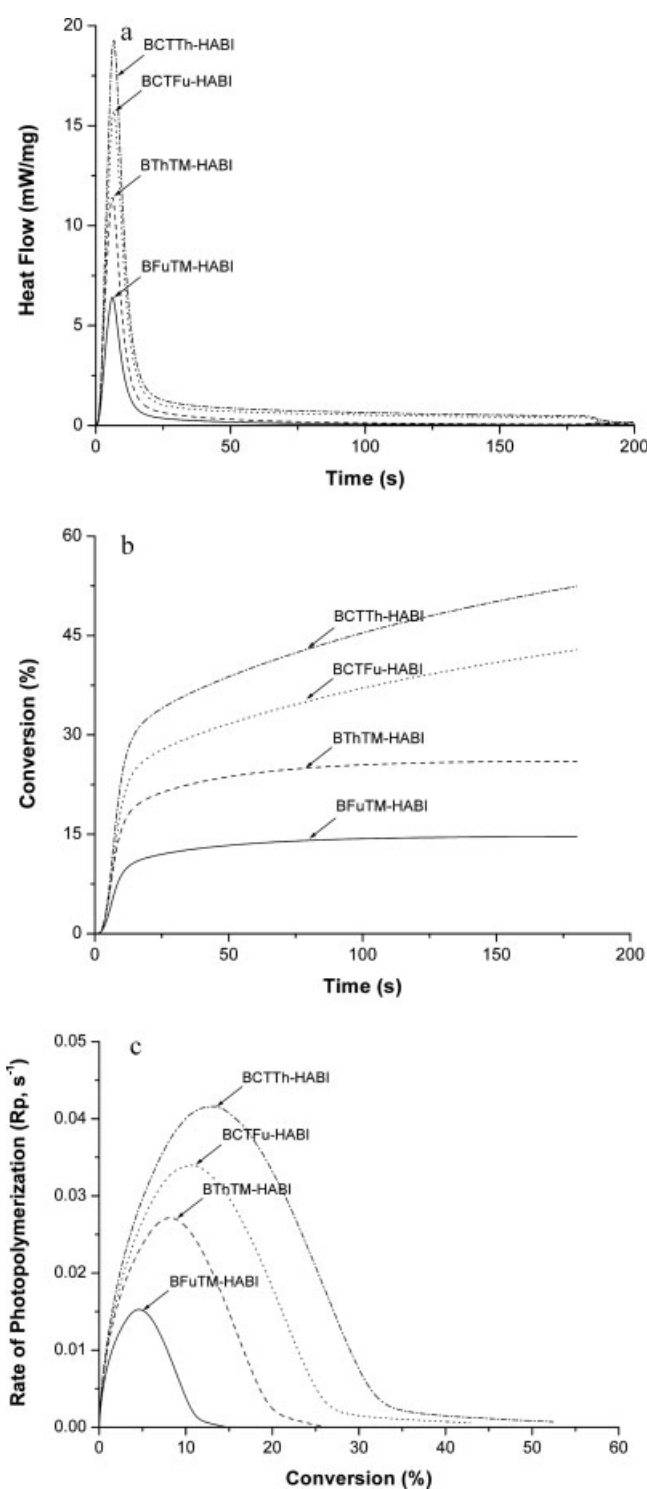


Figure 6 Heatflow versus time curves of TMPTA (a), conversion versus time curves of TMPTA (b) and R_p versus conversion curves of TMPTA, (c) initiated by BFuTM-HABI/MBO, BThTM-HABI/MBO, BCTFu-HABI/MBO, and BCTTh-HABI/MBO systems, irradiated for 3 min at 25°C with a 50 mW/cm² light intensity under a 50 mL/min nitrogen flow.

BCTFu-HABI/MBO and BCTTh-HABI/MBO can initiate efficiently the photopolymerization of PPGDA, but BFTuM-HABI/MBO and BThTM-HABI/MBO can only initiate the photopolymerization of PPGDA slowly. The amount of 2-sulfurbenzoxazole radicals and their diffusion in PPGDA influence corporately the initiation efficiency of HABI/MBO system.

As shown in Figure 5(b,c), the conversions and polymerization rates of PPGDA initiated by BCTFu-HABI/MBO and BCTTh-HABI/MBO systems are much higher than those of BFTuM-HABI/MBO and BThTM-HABI/MBO systems. It is ascribed to the larger amounts of 2-sulfurbenzoxazole radicals in BCTFu-HABI/MBO and BCTTh-HABI/MBO systems. Moreover, weakly polar triarylimidazolyl radicals dissociated from BFTuM-HABI and BThTM-HABI would be incompatible with polar acrylate derivatives such as PPGDA, which hinders their diffusion in PPGDA and results in their inferior yields of 2-sulfurbenzoxazole radicals consequently.

Photopolymerization of TMPTA

Photopolymerizations of TMPTA initiated by BFTuM-HABI/MBO, BThTM-HABI/MBO, BCTFu-HABI/MBO, and BCTTh-HABI/MBO systems are shown as Figure 6(a–c). Figure 6(a) indicates that BCTFu-HABI/MBO and BCTTh-HABI/MBO can initiate efficiently the photopolymerization of TMPTA, but BFTuM-HABI/MBO and BThTM-HABI/MBO can yet initiate the photopolymerization of TMPTA tardily.

Coincidentally with the photopolymerization of PPGDA, the amount of 2-sulfurbenzoxazole radicals and their diffusion in TMPTA affect corporately the initiation efficiency of HABI/MBO system. According to Figure 6(b,c), the conversions and polymerization rates of TMPTA initiated by BCTFu-HABI/MBO and BCTTh-HABI/MBO systems are much higher than those of BFTuM-HABI/MBO and BThTM-HABI/MBO systems. It is attributed to the larger amounts of

2-sulfurbenzoxazole radicals in BCTFu-HABI/MBO and BCTTh-HABI/MBO systems.

CONCLUSIONS

1. Four novel heterocyclic hexaarylbiimidazoles, BFTuM-HABI, BThTM-HABI, BCTFu-HABI, and BCTTh-HABI were synthesized to enhance the UV-vis absorption abilities of hexaarylbiimidazoles.
2. Photochemical behavior measurements approved their high UV-vis absorbance and weak fluorescence emission. ESR detections indicate that the amounts of 2-sulfurbenzoxazole radicals in BCTFu-HABI/MBO and BCTTh-HABI/MBO systems are much larger than those in BFTuM-HABI/MBO and BThTM-HABI/MBO systems.
3. BCTFu-HABI/MBO and BCTTh-HABI/MBO systems exhibit better initiation activities for acrylate derivatives with different functionalities, MMA, PPGDA, and TMPTA, than those of BFTuM-HABI/MBO and BThTM-HABI/MBO systems.

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