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Hierarchically porous π-conjugated polyHIPE as a heterogeneous photoinitiator for free radical polymerization under visible light†

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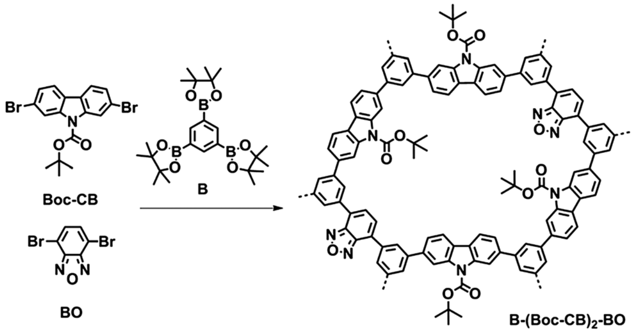
A hierarchically porous π-conjugated polyHIPE was used as a heterogeneous visible light photoinitiator for the radical polymerization of methyl methacrylate (MMA) under a household energy saving light bulb at room temperature. The heterogeneous nature of the porous polymer ensures easy separation and reusability.

Photopolymerization has demonstrated its advantages and played an important role in various industrial applications such as coatings, adhesives, optical waveguides, microelectronics, dental fillings, and other biomaterials for bone and tissue engineering.[1–4] In the past, numerous efficient photoinitiators with different absorption ranges for free radical polymerization were developed. However, they mainly absorb in the UV range.[5] Taking nature as a role model, researchers have put tremendous effort in developing new photocatalysts which absorb mainly in the visible range of light. Many of the photocatalysts have established notable prominence in applications such as water splitting, solar energy storage, and photovoltaics.[6–8] Among the visible light photocatalysts, rare metal complexes, especially ruthenium complexes, have found prominent use due to their synthesis, stability and photoredox properties.

However, the high cost and toxicity of those rare metals, as well as their limited availability, present a huge challenge in their sustainability. Therefore, there has been growing interest in developing metal-free photocatalysts in the field of visible light photocatalysis. In recent years, a number of organic chromophores and dyes were employed successfully in photoredox catalysis.[9–11] Examples of some well-studied photoinitiators that perform in the visible range include titanocene, camphorquinone, organic ketones containing germanium, iridium complexes, and organic dyes.[12–19] Despite their high initiation efficiency, strong odor, toxicity, and high migration are often observed with these low-molar-mass photoinitiators and the homogeneous nature makes them difficult to remove. One method to tackle such problems is to use macromolecular photoinitiators.[20–23] Recently, Kiskan *et al.* reported the use of a phenolphthalein-based microporous polymer network[24] and mesoporous graphitic carbon nitride as metal-free heterogeneous visible light photoinitiators.[25]

High internal phase emulsion (HIPE) polymerization is a relatively new technique that has found a wide variety of applications in tissue engineering scaffolds, enzyme immobilization, gas storage and separation media.[26–29] Very recently, π-conjugated polyHIPEs combine the hierarchically interconnected pore structure of polyHIPEs and the π-conjugated polymer backbone throughout the network, showing high efficiency as a heterogeneous photosensitizer for singlet oxygen generation under visible light.[30] In our previous study, we reported the micropore engineering and photocatalytic activity of conjugated microporous polyHIPEs for highly selective oxidation of organic sulfides to sulfoxides under visible light.[31]



Scheme 1 Synthesis route to B–(Boc-CB)$_2$–BO using palladium catalyzed Suzuki–Miyaura cross-coupling reaction *via* high internal phase emulsion (HIPE) polymerization and its idealized structure. Reaction conditions: Pd(PPh$_3$)$_4$, K$_2$CO$_3$, Span® 80, H$_2$O–toluene, 80 °C, 12 h.

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In this study, we report for the first time the use of a π-conjugated polyHIPE B–(Boc-CB)$_2$–BO (Scheme 1) as a heterogeneous, visible light photoinitiator in the free radical polymerization of methyl methacrylate (MMA). *Via* high internal phase emulsion (HIPE) polymerization, the π-conjugated polymer B–(Boc-CB)$_2$–BO was synthesized *via* palladium-catalyzed Suzuki–Miyaura cross-coupling reactions using *tert*-butylcarbonate functionalized dibromocarbazole (Boc-CB) with 1,3,5-benzenetriboronic acid tris(pinacol) ester (B) as the cross-linker combined with a strong electron acceptor, dibromobenzoxadiazole (BO). The chemical structure, morphology, and optical properties of the porous polymer were characterized by Fourier transform-infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), diffusive reflectance (DR) UV/Vis spectroscopy, solid-state ^{13}C magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy, and N_2 gas sorption measurements.

The system formed stable emulsions that resulted in a monolithic polymer with an interconnected pore structure (Fig. 1a and b). The polymer was insoluble in all common organic solvents tested. The SEM images show that the conjugated polyHIPE has a hierarchical pore structure, consisting of micrometer scale cavities, submicron scale interconnected pores, as well as nanometer scale micropores measured by the N_2 gas sorption experiment (Fig. S5 and S6†). The Brunauer–Emmett–Teller (BET) surface area, micropore size, and total pore volume were measured to be 82 m^2 g^{-1}, 1.5 nm and 0.128 cm^3 g^{-1}, respectively.

Solid state ^{13}C/MAS NMR spectra show chemical shifts at δ = 30, 85 and 155 ppm, which are assigned to the –CH$_3$, quart.-C and >C=O groups of the Boc moiety. The signals between 110 and 150 ppm can be assigned to the aromatic rings in the polymer backbone (Fig. S7†). Thermal gravimetric analysis (TGA) measurements showed that the conjugated network remained intact up to 700 °C, the weight loss at around 200 °C can be attributed to the Boc functional group (Fig. S4†). Fig. 1c displays the very broad absorption band in the visible light range, an optical band gap of 2.16 eV can be derived from the absorption edge. The exhibited baseline increases with decreasing wavelength. This is an indication of light scattering inside the porous structure with sizes in the range of the visible wavelengths. B–(Boc-CB)$_2$–BO exhibited weak emission with a maximum at about 540 nm (Fig. 1d), a large Stokes shift occurred, which indicates a better π–π* transition in the exited state of the polymer.

To demonstrate the photocatalytic activity under visible light, B–(BOC-CB)$_2$–BO was employed to initiate the free radical photopolymerization of methyl methacrylate (MMA) in 50 wt% THF solution using a 23 W household energy saving light bulb at room temperature. Et$_3$N was used as a co-initiator. The set-up is shown in Fig. S8 of the ESI.† A kinetic plot of the radical polymerization of methyl methacrylate (MMA) initiated by B–(Boc-CB)$_2$–BO under visible light at room temperature is shown in Fig. 2.

It shows that the polymerization rate slowed down after reaching *ca.* 80% conversion, exhibiting the character of an

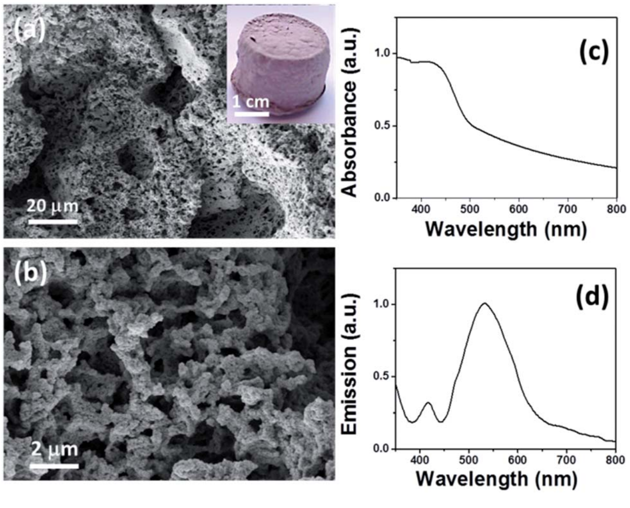


Fig. 1 (a and b) SEM images of B–(Boc-CB)$_2$–BO, the inset is a photograph of the monolithic polymer, (c) DRS UV/Vis, and (d) photoluminescence spectra.

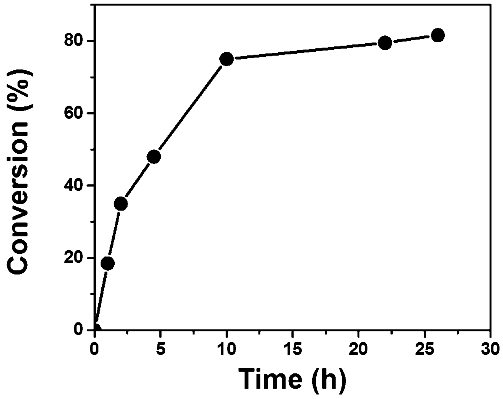
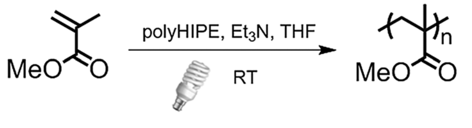


Fig. 2 Photopolymerization of methyl methacrylate using B–(Boc-CB)$_2$–BO as a heterogeneous photoinitiator at room temperature under visible light.

Table 1 Visible light initiated free radical polymerization using B–(Boc-CB)$_2$–BO as a photoinitiator at room temperature



Sample	$h\nu$	Conv. (%)	M_n (g mol^{-1})	M_w/M_n
Blank[a]	—	—	—	—
Blank[b]	+	—	—	—
Blank[c]	+	—	—	—
B–(Boc-CB)$_2$–BO	+	82	34 300	2.67
B–(Boc-CB)$_2$–BO	+	35	12 700	2.18
B–(Boc-CB)$_2$–BO	+	35	8300	1.92

[a] No light with polyHIPE and coinitiator. [b] No coinitiator with polyHIPE and light. [c] No polyHIPE with light and coinitiator. Conditions: MMA (1 mL, 9.39 mmol), B–(Boc-CB)$_2$–BO (25 mg) and Et$_3$N (30 mg) in 50 wt% THF.

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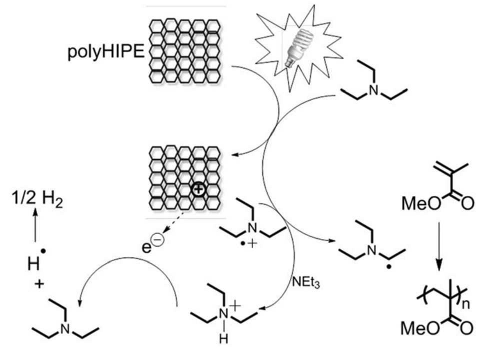

Fig. 3 Suggested mechanism of photoinitiation using conjugated porous polyHIPE under visible light.

exponential development. In this case a second kinetic order might have occurred. Table 1 presents the characterization data of the PMMA polymers obtained at different conversions including control experiments. Both the initiating components, namely, polyHIPE and Et_3N, are indispensable, no polymerization was observed when either component was absent. An acceleration of the conversion, the so-called Trommsdorff effect, was not observed. The reason could be that the polymerization was conducted in 50 wt% THF solution with vigorous stirring, both of which alleviate the system with a sudden localized viscosity increase.

Control experiments conducted without light irradiation resulted in no polymer formation. In Fig. 3, we suggest an initiation mechanism similar to that in the literature.[25] Under visible light irradiation, charge separation inside the conjugated polyHIPE occurred,[32] which likely could be stabilized within the nanometer-sized pores. Et_3N was oxidized by the hole inside the conjugated polyHIPE into the corresponding radical cation. Another Et_3N molecule formed consequently a free radical after giving away one proton to a radical cation. The radical polymerization of MAA was initiated. Followed by the photoinitiation an electron could react with the amine cation, forming a neutral amine and a hydrogen radical.

Furthermore, to investigate the reusability of B–(Boc-CB)$_2$–BO as a heterogeneous photoinitiator, three additional repeating experiments of photopolymerization were performed under the same reaction conditions in a large time scale of 24 h (Fig. S12†). PMMA was obtained without a significant loss of conversion, demonstrating the stability and reusability of the polyHIPE. The SEM image of B–(Boc-CB)$_2$–BO after the third run still showed a similar porous structure, indicating promising stability of the conjugated polyHIPE (Fig. S9†). However, the efficiency of photoinitiation of this new-class conjugated porous polymer is still unknown; new photophysical studies are being conducted in order to gain more understanding and optimization of the system.

Conclusions

In summary, photopolymerization of MMA using π-conjugated porous polyHIPE as a heterogeneous photoinitiator could be efficiently achieved under visible light. A household energy saving light bulb was used as a light source, which provides an economically low-cost solution. The hierarchical porosity of the conjugated polyHIPE could be advantageous in attaining efficient mass transfer in the catalytic reactions. The heterogeneous nature and the stable 3D structure of polyHIPE allow its facile removal from the polymerization mixture and reusability without a significant loss of activity. Moreover, the π-conjugated polyHIPE-based photoinitiator minimizes odor, toxicity and migration problems, which usually accompany the low molar mass photoinitiators.

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