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Hierarchically Porous Π-Conjugated PolyHIPE as Heterogeneous Photoinitiator for Free Radical Polymerization under Visible Light

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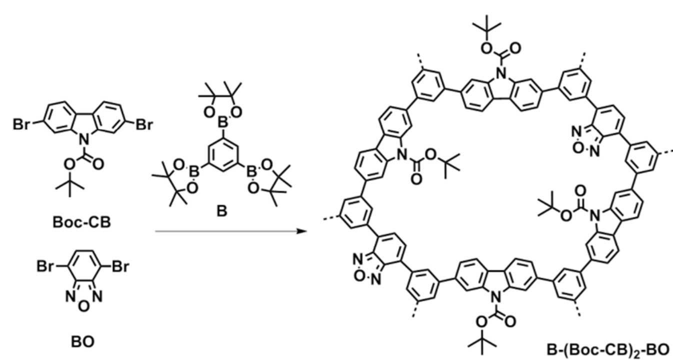
Abstract: A hierarchically porous π-conjugated polyHIPE was used as heterogeneous visible light photoinitiator for the radical polymerization of methyl methacrylate (MMA) under a household energy saving light bulb at room temperature. The heterogeneous nature of the porous polymer ensures easy separation 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 large 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 seen a growing interest in developing metal-free photocatalysts in the field of visible light photocatalysis. In recent year, a number of organic chromophores and dyes were employed successfully in photoredox catalysis.[9-11] Examples of some well-studied photoinitiators acting 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 a mesoporous graphitic carbon nitride as a metal-free heterogeneous visible light photoinitiator.[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 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 with visible light.[31]



Scheme 1. Synthetic route and idealized structure of B-(Boc-CB)$_2$-BO using palladium catalyzed Suzuki-Miyaura cross-coupling reaction via high internal phase emulsion (HIPE) polymerization. Reaction conditions: $Pd(PPh_3)_4$, K_2CO_3, Span® 80, H_2O/toluene, 80 °C, 12 h.

In this study, we report the first 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-

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Miyaura cross-coupling reactions using tert-butylcarbonate funtionalized 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 (Figure 1a and 1b). The polymer was insoluble in all common organic solvents tested. The SEM images showed 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 (Figure S5 and S6). The Brunauer-Emmett-Teller (BET) surface area, micropore size, and total pore volume measured are 82 m^2 g^{-1}, 1.5 nm and 0.128 cm^3 g^{-1}, respectively.

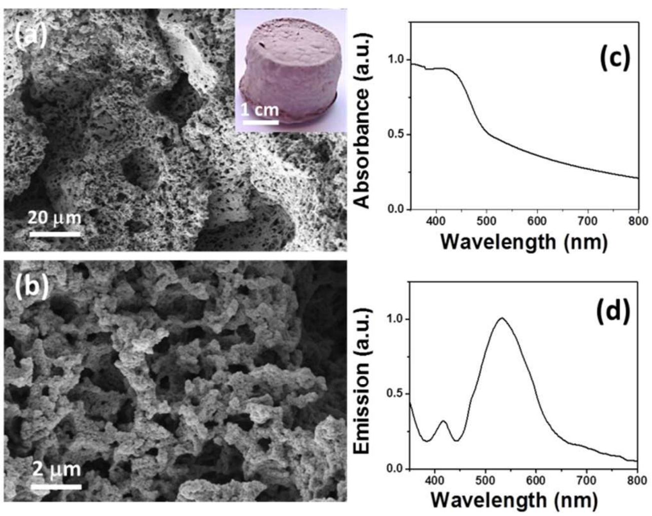

Figure 1. (a) and (b) SEM images of B-(Boc-CB)$_2$-BO, the insert is a photograph of the monolithic polymer, (c) DRS UV/Vis, and (d) photoluminescence spectra.

The solid state ^{13}C/MAS NMR spectroscopy showed chemical shifts at $\delta = 30$ and 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 (Figure 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 (Figure S4). Figure 1c displays 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 (Figure 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_3N was used as a co-initiator. The set-up is showed in Figure S8 of the supporting information. 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 Figure 2.

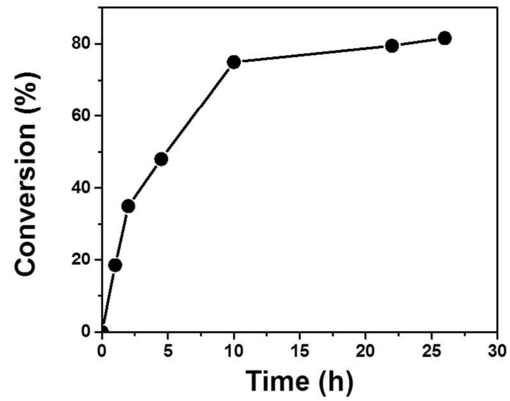

Figure 2. Photopolymerization of methyl methacrylate using B-(Boc-CB)$_2$-BO as heterogeneous photoinitiator at room temperature under visible light.

It shows that the polymerization rate slowed down after reaching ca. 80% conversion, exhibiting the character of an 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 of the initiating components, namely, the 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 from sudden localized viscosity increase.

Table 1. Visible light initiated free radical polymerization using B-(Boc-CB)$_2$-BO as 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	34300	2.67
B-(Boc-CB)$_2$-BO	+	35	12700	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_3N (30 mg) in 50 wt% THF.

Control experiments conducted without light irradiation resulted in no polymer formation. In Figure 3, we suggest a similar initiation mechanism in the literature.[25] Under visible light irradiation, a 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 radical cation. The radical polymerization of MAA was initiated. And the electron followed by the photoinitiation could reaction with the amine cation, forming neutral amine and hydrogen radical.

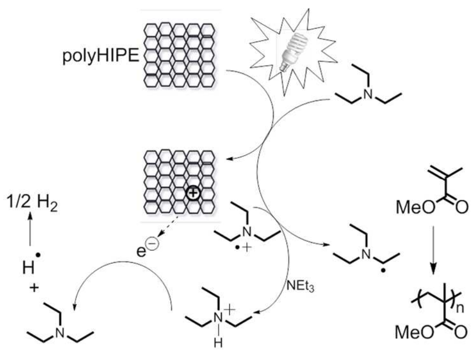

Figure 3. Suggested mechanism of the photoinitiation using conjugated porous poylHIPE under visible light.

Furthermore, to investigate the reusability of B-(Boc-CB)$_2$-BO as heterogeneous photoinitiator, three additional repeating experiments of the photopolymerization were performed under the same reaction conditions in a large time scale of 24 h (Figure S12). PMMA was obtained without 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 a promising stability of the conjugated polyHIPE (Figure S9). However, the efficiency of the 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 heterogeneous photoinitiator could be efficiently achieved under visible light. A household energy saving light bulb was used as 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 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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