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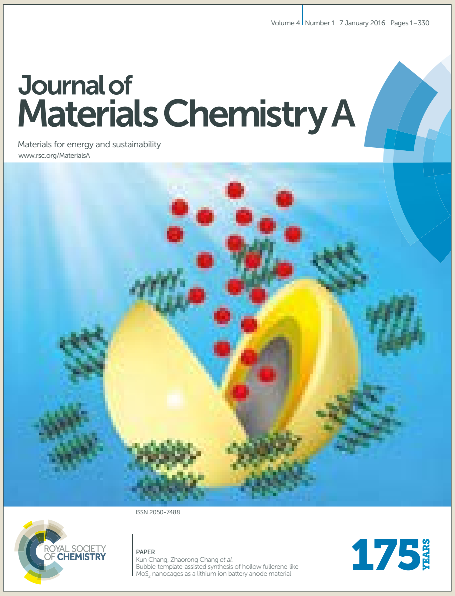

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COMMUNICATION

Efficient Photocatalytic Oxidation Sensitized by Conjugated Polymers in Batch and Microreactors under Visible Light

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We studied microfluidic reaction systems for the efficient catalytic oxidation of α-terpinene sensitized by conjugated polymers. Different microreactors, including flow-reaction-based mono- and dual-channel, as well as polymer-coated dual-channel microreactors, were designed and evaluated, which demonstrated improved reaction efficiency.

Singlet oxygen ($^1O_2$) is an important reactive oxygen species (ROS) that plays an important role in many physiological processes in living systems and acts as an excellent oxidizing agent in various organic reactions.[1-3] Due to its high oxidation efficiency, sustainability, and convenience in separation, singlet oxygen has been widely used in organic synthesis, including the preparation of endoperoxides from Diels–Alder reactions,[4] dioxetanes from [2+2] cycloadditions,[5] hydroperoxides from alkenes and phenols,[6] sulfoxides from sulfides,[7] phosphine oxides from phosphines,[8] and selective oxidation of aromatic alcohols into corresponding aldehydes.[9] Moreover, some reactions involving singlet oxygen provide regio-specific and stereo-specific introduction/insertion of oxygen into organic substrates, such as in ene reactions with allylic alcohol substrate.[10, 11]

$^1O_2$ is usually produced by photosensitization or chemical reactions. Commonly used photosensitizers include transition metal complexes, organic dyes and porphyrin derivatives,[12, 13] which can transfer electronic energy from a triplet excited state to ground state triplet oxygen. However, there are some intrinsic drawbacks associated with these compounds, such as toxicity and photo-bleaching problems. Recently, a growing number of novel materials have been developed as photosensitizers, including microporous polymers (MPs),[14, 15] mesoporous graphitic carbon nitride,[16, 17] silicon nano crystals,[18] metal–organic frameworks (MOFs),[19] and conjugated polymers (CPs).[20] CPs have attracted a great deal of attention due to their potential applications in organic solar cells, chemical sensors, cell imaging, and a variety of other fields.[21-23] It has been reported that some CPs are able to generate singlet oxygen upon light irradiation through intersystem crossing (ISC) leading to CPs' anti-bacteria and anti-tumor applications.[24-30] However, no studies have reported the use of CPs as $^1O_2$ photosensitizers in organic synthesis.

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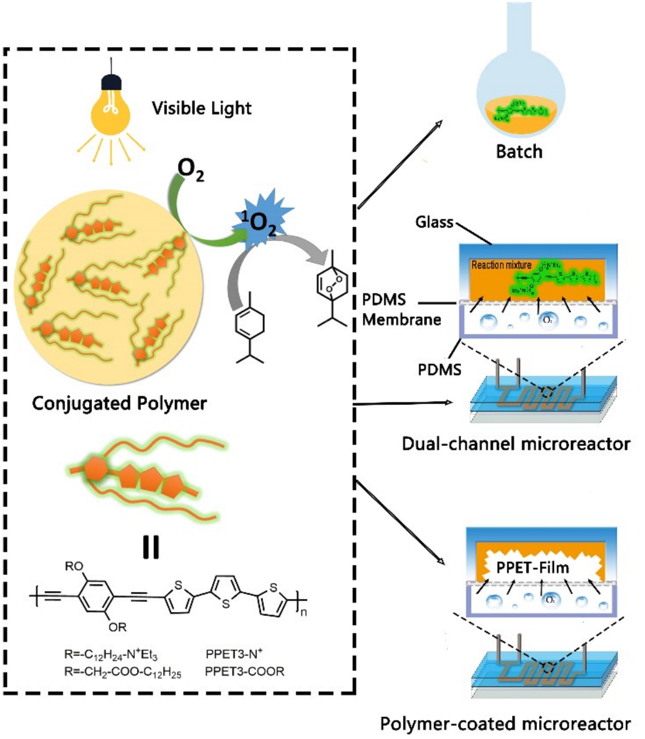

Scheme 1. Schematic illustration of PPET3 photosensitized oxidation of α-terpinene in a batch, a dual-channel microreactor, and a polymer-coated microreactor.

Herein, we report an efficient photocatalytic oxidation of α-terpinene sensitized by conjugated polymers, PPET3, in a batch reaction and microreactors. Different microreactors were designed, including flow-reaction-based microreactors as well as a polymer-coated dual-channel microreactor (Scheme 1).

Two poly (p-phenylene ethynylene terthiophenes) (PPET3s), PPET3-N$^+$ and PPET3-COOR (structures are shown in Scheme 1), were designed and synthesized. Conjugated polymer backbones have been known to contribute to light-harvesting properties. Meanwhile, the terthiophenes units were introduced in backbones, which have been reported to enhance ISC efficiency due to heavy atom effect of sulfur.[31-37] In particular, improved singlet oxygen generation of PPET3-N$^+$ and its photocytotoxicity to tumor cells were observed,[38] which motivated our further exploration of these polymers in photocatalytic reactions.

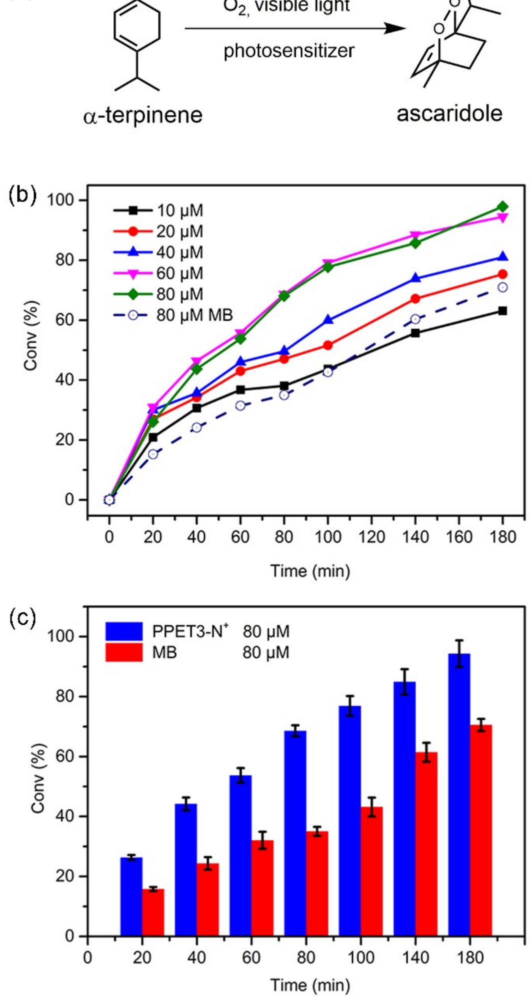

Figure 1. (a) Oxidation of α-terpinene by singlet oxygen via the Diels-Alder [4+2] reaction; (b) Photosensitized conversion of α-terpinene into ascaridole in batch reaction; (c) Comparison of the photocatalytic efficiency between PPET3-N+ and methylene blue (MB). Conversion was analyzed using UV/Visible spectroscopic measurements. Reaction conditions: 0.1 M α-terpinene with different concentrations of PPET3-N+ or 80 μM methylene blue in 5 mL ethanol under 120 W white LED light irradiation for different lengths of time periods.

To investigate the activity of PPET3-N$^+$ as a photosensitizer to produce singlet oxygen, photo-oxidation of α-terpinene to ascaridole (Figure 1) in the presence of PPET3-N$^+$ was evaluated under white LED light. Photocatalytic reaction mechanism of α-terpinene has been reported and studied in details. Generally speaking, singlet oxygen can catalyze a [4+2] photooxidation of α-terpinene to form the main product as ascaridole, and byproducts including p-cymene and allylic epoxides of α-terpinene, which might be formed due to likely successor reactive oxygen intermediates.[2, 39, 40] In our study, absorbance at a maximum wavelength of 265 nm was used to quantify the remaining α-terpinene during the photo-oxidation process in both ethanol and acetonitrile (Figure S1 in the Supporting Information). To intuitively reflect the capability of PPET3-N$^+$, this reaction was carried out with methylene blue (MB), a commercially available small molecular photosensitizer, as a reference substance in the same conditions. As depicted in

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Figure 1b and 1c, with 80 μM PPET3-N$^+$ after 3 h of reation time (entry 9 in Table 1), 95% α-terpinene was converted into ascaridole with a yield of about 93%, as revealed by NMR spectroscopy. It is noteworthy to point out that no other significant by-product was found, which indicates the high specificity of the reaction and further confirms that the oxidizing agent was singlet oxygen rather than other reactive oxygen species like ·OH or H_2O_2.[9] Comparatively, only about 70% conversion of α-terpinene using MB as the photosensitizer was obtained after 3.0 h, suggesting that PPET3-N$^+$ exhibits higher photo-catalytic activity than MB under visible light.

Reaction conditions were optimized using different concentrations of PPET3-N$^+$ and different light intensities (Figure S2 in the Supporting Information). When the concentration of PPET3-N$^+$ increased from 10 to 60 μM, the conversion of α-terpinene went up correspondingly. However, as the concentration increased past 60 μM, subtle differences in the reaction rate were observed. As mentioned previously, the production of singlet oxygen is related to the energy transfer process from the triplet photosensitizer to triplet oxygen. As concentration ascends, the probability of intermolecular collisions of excited state PPET3-N$^+$ also increase and influence ISC and the production of the triplet photosensitizer.[41, 42] One possibility of this phenomenon is that higher concentrations of photosensitizers result in an increased scattering effect, which reduces the UV light penetration.[43] Light intensity demonstrated to be another influencing factor, where the conversion of α-terpinene with 80 μM PPET3-N$^+$ was improved from 0% to 60% and to 94%, as from the non-flashlight irradiation to the light intensity of 70 W and 120 W, respectively, using a white LED light. Thus, the stronger light source promoted higher photosensitization efficiency.[44] Meanwhile, the photostability experiments (Figure S3) suggested that both polymers, PPET3-N$^+$ and PPET3-COOR, were quite stable in the batch reaction under white LED light with only about 10% intensity variations.

We further explored the behavior of PPET3-N$^+$ in different microreactors. The use of microreactors for chemical reactions has received considerable attention in recent years.[45, 46] Compared to traditional batch systems, microreactors have been reported to have large surface area to volume ratios to ensure thermal homogeneity, have improved heat and mass transfer to produce faster reactions, and maintain safe and convenient reactions.[47, 48] Several properties of microreactors have made them excellent candidates for photoreactions, including good spatial illumination homogeneity, gas permeability, light transmission, and high-illuminated surface area per unit volume.[49-51] Both mono- and dual-channel microreactors were designed and fabricated, as shown in Figure 2. A mono-channel microreactor was fabricated on glass substrates due to its excellent compatibility and stability with organic solvents.[52] The channel consisted of a circular mixer and long serpentine section to ensure maximum mixing and increase utilization of space. Typically, the glass substrates are irreversible bonded with another glass plate by means of a thermally annealed method to obtain an integrated device; however, this method requires high temperatures and precise control. Therefore, polydimethylsiloxane (PDMS), an inexpensive, transparent and accessible material, was used to replace the glass plate to attach glass substrates following plasma treatment. Nonetheless, the mono-channel microreactor presents the inherent problem of controlling the heterogeneous gas-liquid reaction to supply sufficient gas for the reaction. To overcome these shortcomings, a dual-channel microreactor was prepared according to a previous report.[53]

The dual-channel microreactor is composed of an upper glass chip for the reaction and a lower PDMS chip for air flow, which are separated by a gas-permeable PDMS membrane. The PDMS membrane affords sufficient air for the reaction and enhances gas-liquid phase contact. In our study, the PDMS membrane was prepared by a spin coating with a rotation speed of 1200 rpm for 30 s to obtain a PDMS film at thickness of 49 μm (Figure S4).

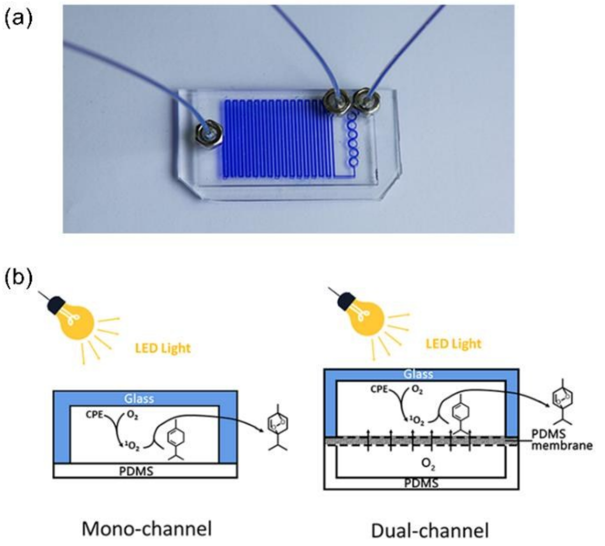

Figure 2. (a) Picture of the dual-channel reactor, which is manufactured with an upper glass chip, lower PDMS chip, and PDMS membrane; (b) Schematic representations of mono-channel and dual-channel microreactors.

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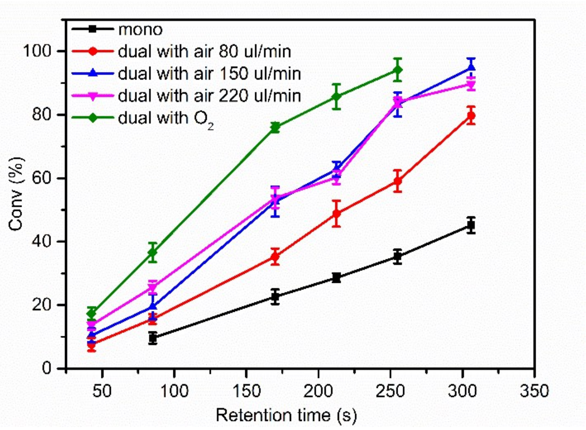

Figure 3. Photosensitized conversion of α-terpinene into ascaridole in the mono-channel and dual-channel microreactors. Conversion was analyzed using UV/Visible spectroscopic measurements. Reaction conditions: 0.1 M α-terpinene with 80 μM PPET3-N$^+$ at different gas flow rates under 61.5 W/cm^2 white LED light irradiation for different lengths of time periods.

Photo oxidation of α-terpinene was conducted at different reaction conditions and analyzed in mono- and dual-channel. According to literature reports, acetonitrile is a better solvent than ethanol for PDMS based microreactors due to swelling problems in organinc solvents.[54] Thus, acetonitrile was further used in reactions on microreactors in our study. The concentrations of α-terpinene and PPET3-N$^+$ were 0.1 M and 80 μM, respectively, and the retention time was adjusted by changing the injection rate. The results are presented in Figure 3. While both mono- and dual-channel microreactors could improve photocatalytic efficiency, dual-channel provided better performance than the mono-channel in terms of conversion at the same retention time. When the conversion in the dual-channel microreactors was over 90% after 5 minutes (entry 3) under an air flow rate of 150 μL/min, only 45% of α-terpinene was oxidized in the mono-channel (entry 1) within the same time period, and much longer time as 3 hours was needed for the similar conversion in batch experiment (entry 9). Moreover, the air flow rate also plays an important role in determining the reaction conversion. When the air flow rate increased from 80 to 150 μL/min, the conversion increased from 80% to 94% within 306 s (entry 3). However, a subtle decreased was observed when the air rate further increased to 220 μL/min (entry 4), which is mostly likely attributed to air saturation in the channels. Furthermore, when O_2 replaced air flow, the conversion reached 90% in 252 s (entry 5). These results clearly demonstrate that dual-channel microreactors profoundly improve the reaction efficiency compared to the mono-channel and batch system. It has also been reported that amplificative microreactors provide excellent conversion and output,[55] suggesting that our proposed method may have further applicability in scale-up reactions.

Recently, there has been an increasing interest in the immobilization of catalysts on microreactors, which show numerous advantageous like uniform dispersion of catalytic active components, prevention of nanocatalysts from deactivation by avoiding aggregation, and simplified workup procedures.[56-58] The strategies of immobilization could be classified into two major types: physical and chemical modifications. Using the physical modification like dip-coating, drop-casting, spray-coating etc.,[59] catalysts are adhered to the surface of channels via electrostatic interaction or Van der Waals' force, whereas chemical modifications are obtained by grafting catalysts on the surface by chemical bonding over a number of chemical processes.[60] It has been revealed that lipid-soluble conjugate polymers exhibit excellent film forming properties and can be applied in sensors and in optoelectronic devices.[61] PPET3-COOR, which has alkyl ester side chains, was used to drop cast a film on a glass channel, due to its good solubitity in organic solvent and excellent spreadability on glass. The polymer film was formed by drop-cast the polymer solution on the glass channel surface. The excess polymer film outside the channel was gently cleaned off, then a PDMS membrane was irreversible bonded between the modified glass and another PDMS piece with channel feature using oxygen plasma treatment. Atomic force microscope (AFM) was used to characterize the morphology of the polymer film.

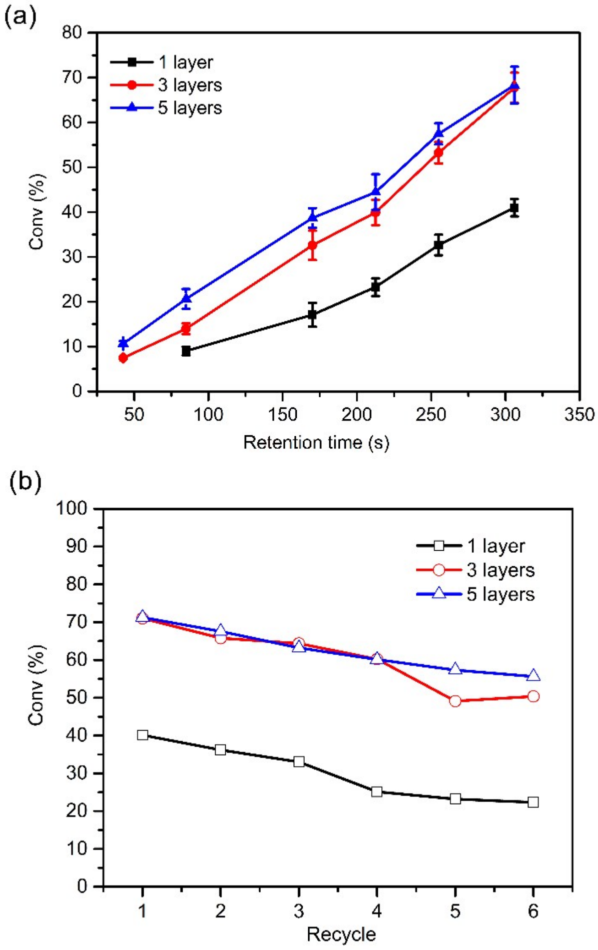

Figure 4. (a) Photosensitized conversion of a-terpinene into ascaridole in PPET3-COOR film coated dual-channel microreactors; (b) Evaluation of the reusability of PPET3-COOR film coated dual-channel microreactors. Conversion was analyzed using UV/Visible spectroscopic measurements. Reaction conditions: 0.1 M α-terpinene, 150 μL/min air flow rate and 5 min of retention time under 61.5 W/cm^2 white LED light irradiation.

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Table 1. Photo-oxidation of α-terpinene in 3 different systems^a.

Entry	Reactor^b	Air	Time	Conv^c
1	Mono-channel	/	5 min	45%
2	Dual-channel	80 μL/min	5 min	80%
3	Dual-channel	150 μL/min	5 min	94%
4	Dual-channel	220 μL/min	5 min	89%
5	Dual-channel	O_2^d	4.2 min	90%
6	1 layer polymer-coated	150 μL/min	5 min	41%
7	3 layers polymer−coated	150 μL/min	5 min	68%
8	5 layers polymer−coated	150 μL/min	5 min	68%
9	Batch	/	3 h	95%

^{a} Reaction conditions: 0.1 M α-terpinene, 120 W white LED light in batch and 61.5 W/cm^2 white light in microreactor , room temperature, ethanol in batch system and acetonitrile in microreactors as the solvent; ^{b} Concentration of PPET3-N$^+$ in experiment were 80 μM; ^{c} Conversions were recorded with UV/Vis spectra analysis; ^{d} Flow with O$_2$.

Figure 4a shows that the polymer-coated microreactor exhibited excellent photocatalytic capability. From obtained data, when channels were coated with 1 layer of polymer film, the conversion of α-terpinene was about 41% in a retention time of 5 min (entry 6). The oxidant efficiency of PPET3-COOR deposited film kept an upward tendency as thickness increased from 1 to 3 layers (entry 7). However, there were no significant changes in the reaction efficiency between 3 and 5 layers. The conversion of α-terpinene with 5 layers of film was slightly higher than that with 3 layers within 5 min, but both conversions were approximately 68% in a retention time of 5 min (entry 8). AFM results (Figure S5) showed that many pores are evenly distributed on the films with increasing pore size from 0.8 to 4 μm as the layers build up. Based on the sectional height figures (Fig. S5 d-f), the thickness of the polymer-deposited film show an upward trend and are 95, 250, and 350 μm for 1, 3 and 5 layers, respectively. The results suggest that the increasing thickness and larger pore size of PPET3-COOR film enhance the photo-oxidation, which might be due to increasing contact of the reactant with the polymer, as well as more efficient singlet oxygen production.

To demonstrate the reusability of polymer-deposited microreactors, repeated experiments were conducted in the same conditions: 0.1 M α-terpinene, retention time of 5 min, and air flow rate of 150 μL/min. The results in Figure 4b show that as the number of tests increased, the reaction conversion showed a descending trend, and the conversion of 1 layer film decreased from 40% to 22% after six experiments. Similarly, the conversion of 3 layers and 5 layers both declined from 70% to about 50% and 55%, respectively. In fact, the effluent reaction solution from the outlet was slightly yellow, as observed by the naked eye. This result should be mainly attributed to the physical adsorption and desorption of polymer film on the glass surface.

In conclusion, we have developed CP-based microreactors to generate $^1O_2$ in photosensitized oxidation. Compared to traditional small molecule photosensitizers, PPET3-N$^+$ exhibited better photocatalytic performance under visible light irradiation. Significant reaction efficiency was achieved by conducting reaction with PPET-N$^+$ in designed dual-channel microreactors. The PPET3-COOR films were sufficiently deposited on the surface of channels to obtain an integrated polymer-coat microreactor, which presented good photocatalytic abilities. In addition, we anticipate to further improve the properties of the polymer-coated microreactor in future studies as a mean to promote its application in continuous photocatalytic organic synthesis systems.

Conflicts of interest

There are no conflicts to declare.

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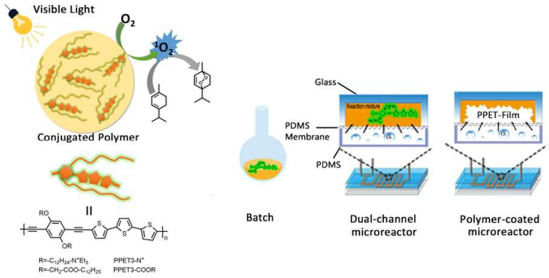

Conjugated polymer photosensitized oxidation of α-terpinene in batch and different microreactors including mono- and dual-channel,and polymer-coated dual-channel microreactors, were studied.