

A TRI-PHASE CATALYTIC MICROFLUIDIC REACTOR FOR THE GENERATION OF SINGLET OXYGEN USING A NOVEL IMMOBILISED *SECO*-PORPHYRAZINE CATALYST

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ABSTRACT

A *seco*-porphyrazine photooxygenation catalyst was co-polymerised within a norbornene based Ring Opening Metathesis Polymerisation (ROMP) gel coating the internal surfaces of a microfluidic reactor. Subsequently, continuous flow photooxidations of α -terpinene were performed in space time yields 100 times faster than bulk equivalent reactions.

Keywords: microreactor, channel derivatisation, catalysis, photooxidation, triphasic reactions

1. INTRODUCTION

Singlet oxygen is a versatile reagent for oxidation reactions with applications including cycloadditions with dienes producing endoperoxides and ene reactions providing allylic hydroperoxides. Currently, the most effective method for singlet oxygen generation is the dye-sensitized photoexcitation of ground-state triplet oxygen. Previous work has focussed on the increased process safety afforded by the generation and use of singlet oxygen within a microfluidic structure using soluble photosensitising dyes.[1] Herein we report the development of an advanced catalytic microfluidic reaction system for the production of singlet oxygen using a tri-phasic system. This incorporates both the oxygen flow and the substrate solution along with a solid supported photosensitizing catalyst confined within the microfluidic structure. Continuous-flow reactions across a polymer immobilised photosensitizing dye produce cleaner transformations with simplified purification.

2. THEORY

Singlet oxygen production using *seco*-porphyrazines has previously been demonstrated with high quantum yields, establishing them as photooxygenation catalysts for the synthesis of endoperoxides from the corresponding dienes. Furthermore, these macrocycles have been reported to be successfully immobilised on resin beads which have efficiently catalysed singlet oxygen production under mild conditions.[2] In many cases the *seco*-porphyrazines proved themselves to be superior catalysts compared with traditional dyes sensitizers, such as Rose Bengal.

In recent years, several techniques for mounting catalysts within chip systems have been developed, and the advantages of catalyst immobilisation within microfluidic devices is well established.[3, 4] However, these systems have not been shown to be resistant to photooxidation, whereas ring opening metathesis polymerisation gels (ROMP gels) are

known to be stable under these conditions. Subsequently, we report a *seco*-porphyrazine catalyst mounted within a microfluidic reactor network using ROMP gel as a solid support.

3. EXPERIMENTAL

The microfluidic reactor featured a network of isotropically etched glass channels, typically with depths of 80 μm and widths of 210 μm . Protruding motifs intermittently dispersed along the channel length enhanced the physical attachment of the ROMP gel to channel surfaces by bulk forces. Functionalised ROMP gel was mounted into the microfluidic channels using localised thermal polymerisation controlled by a resistive heating network (Figure 1).

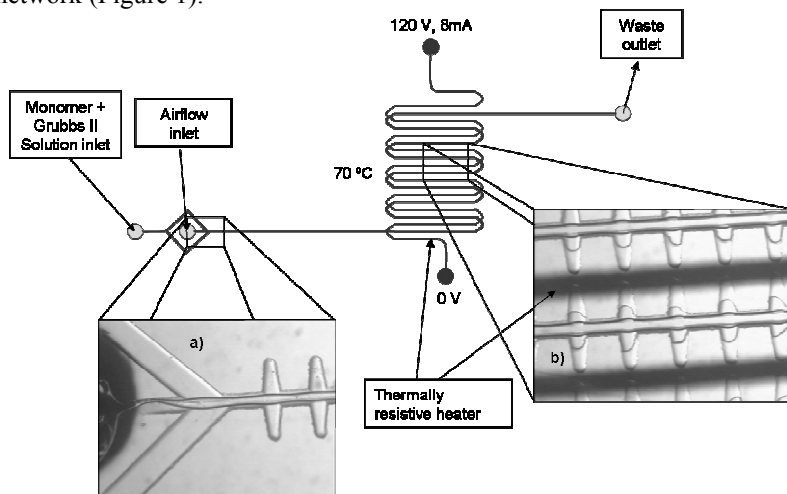


Figure 1. Experimental Schematic for ROM polymerisation derivatisation. a) Interface between air flow and “jacketing” polymerisation solution b) Micro channels illustrating tri-phasic system as polymer forms, polymer in “motifs” extremities then liquid co-monomer solution jacketing air flow.

The channel was maintained by flowing monomer solution in annular flow with a concurrent flow of compressed air. Visualisation by the co-polymerisation of a fluorescent monomer within the ROMP gel illustrated an even and continuous channel coating (Figure 2).

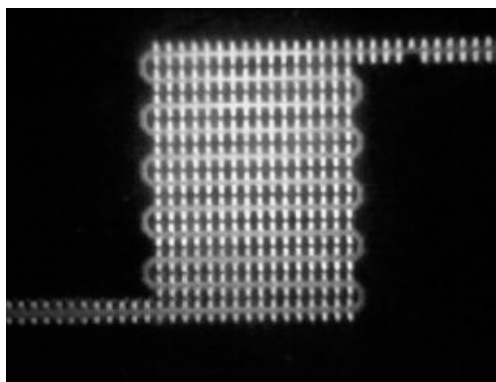


Figure 2. Wall coating of microfluidic device visualised using a fluorescent marker.

4. RESULTS AND DISCUSSION

Incorporation of *seco*-porphyrazine labelled gel (Figure 3) resulted in a wall coating averaging 7 μm .

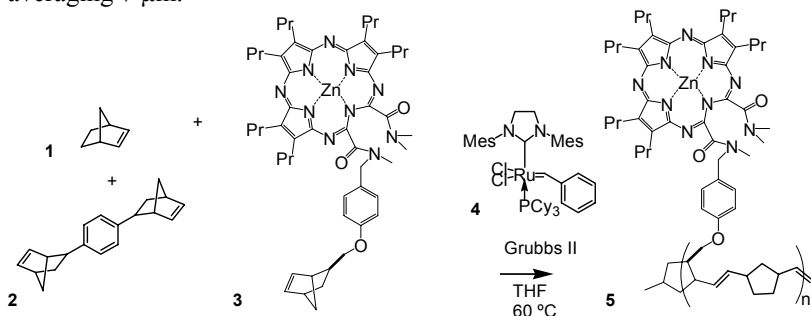


Figure 3. Synthesis ROM polymer functionalised with *seco*-porphorazine.

Oxygen and a solution containing 0.021M α -terpinene in dichloromethane were combined in slug flow at an overall flow rate of 7.7 $\mu\text{l min}^{-1}$ giving a residence time on chip of 15.5s. Transformation of α -terpinene to ascaridole (Figure 4) was monitored by GC and gave space time yields in excess of 0.45% s^{-1} . Reactions carried out in bulk using the same polymer gave space time yields of 0.0041% s^{-1} . The increase in relative space time yields can be attributed to the increased rate of mass transport of oxygen into the catalytic system in a microfluidic environment.

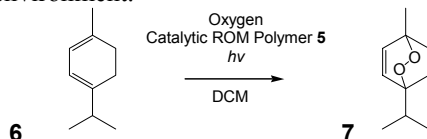


Figure 4. Photooxygenation of α -terpinene to ascaridole.

5. CONCLUSIONS

The increase in relative space time yields can be attributed to the increased rate of mass transport of oxygen into the catalytic system in a microfluidic environment. Coating microfluidic reactors with this *seco*-porphyrazine labelled polymer, and performing continuous flow photo-oxidations provided significant increases in efficiency relative to bulk scale reactivity. This improved reactivity demonstrates the benefits of continuous flow microfluidic reactors for multiphase catalysis and photocatalytic applications.

ACKNOWLEDGEMENTS

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