Functional Monoliths for Flow Processes by RAFT Polymerisation

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Introduction
Polymeric monoliths have recently emerged as a new class of solid supports for stoichiometric and catalytic reactions in continuous flow synthesis.[2] We sought to use Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerisation to synthesise these monoliths: RAFT provides control over polymer-chain growth in linear radical polymerisation, and should provide control over pore size distribution and functionality distribution in crosslinking polymerisation. This work aims to develop such solid supports, in order to target important reactions for the pharmaceutical industry (eg. amide coupling).[2]

Monolith synthesis and characterisation
The process of monolith synthesis uses a high proportion of crosslinkers and a poor solvent deliberately chosen to behave as a porogen: these conditions are quite different to those “typical” polymerisations in which RAFT has been utilized. Using 2-cyano-2-propyl dodecyl thiocarbonate as a RAFT agent, we recently found that suitable polystyrene monoliths were obtained when 0.4 to 2 equivalents of RAFT / AIBN were used.[2]

A linear relationship between backpressure and flow rate was obtained when MeOH or CHCl₃ was pumped through the monoliths, indicating laminar flow of liquid through the material.

Monolith-bound RAFT end-groups
Reaction with hydrazine
The solid-bound thiocarbonylthio groups are available for heterogeneous reaction in a flow setting, as shown by reaction with hydrazine.[4]

The monolith decolourised and an aliphatic C12 residue due to the reacted RAFT group was detected in the reaction solution. Using a monolith made with RAFT/AIBN = 4, the amount of available RAFT groups was quantified by elemental analysis. Since a third of sulfur remained in the monolith after treatment with hydrazine, the end groups are quantitatively available for reaction in a swelling solvent such as THF.

Post-reaction, a qualitative assay with 2,2’-dipyridyl disulphide[2] demonstrated the presence of thiol functionality on the monolith.

Surface grafting
To develop a potential solid-supported catalyst, poly(vinylphenylboronic acid) was successfully grafted onto a monolith using the RAFT end groups.

Conclusions
Monolith synthesis with a RAFT agent enables control of pore size and polymer globules, while maintaining good flow properties. Our synthetic protocol provides a convenient route to monoliths containing RAFT end-groups, which are accessible for surface modification or grafting reactions. These reactive groups provide a platform for introducing a wide range of functionality. The utility of these grafted monoliths as catalysts in flow synthesis are currently being explored.

REFERENCES

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