EXPLOITING THE ADVANTAGES OF THALESNANO INSTRUMENTS IN CONTINUOUS FLOW POLYMERIZATIONS

INTRODUCTION

Designing and synthesizing functional and unique materials that can be fine-tuned for a wide range of applications are key aspects in the polymer industry. Continuous flow technologies provide convenient solutions for scalability, reaction control and streamlining the material design process by circumventing purification steps that are common in traditional batch polymerization procedures. Surfactants and dispergants used in industrial wastewater treatment are two examples of the many uses of terminally functional polymers[1].

The two research papers featured in this application note provide great insight into the uses of continuous flow technology in the fields of polymerization and polymer functionalization. Rigoberto Advincula and his team achieved highly efficient RAFT polymerization, feasible for exploring uses in energy storage materials in a Phoenix Flow Reactor system[2]. David M. Haddleton and his group utilized an H-Cube® Pro to hydrogenate end-functional polymyrcene and polyisoprene with the aim of further improving stability[3].

INSTRUMENTATION AND SAFETY CONSIDERATIONS

Used in the RAFT polymerization experiments the Phoenix Flow Reactor, paired with the Pressure Module and HPLC Pump provide a platform for homogeneous and heterogeneous catalytic reactions up to 200 bar and 450 °C. CAN communication between the Pressure Module and the Phoenix Flow Reactor lets the user observe and manipulate the reaction pressure straight from the magnetically attached screen of the Phoenix. The built-in pressure sensor and external temperature measurement points provide further insight into reaction stability and kinetics. Broadening the scope of reactions, the modularity of ThalesNano systems offers the possibility to connect multiple liquid and gas feeds, including H-Genie® on-demand hydrogen generators to the Phoenix Flow Reactor.

The reactor can house a multitude of different sized Metal-Metal Sealed (MMS) columns, designed to be filled with solid catalysts. Various sizes of coiled loops are also available to carry out homogeneous catalytic reactions in the Phoenix. Every part of a Phoenix Flow Reactor system can be remotely controlled and automated using the THS System Controller®, allowing the user to specify customized safety triggers across a whole reactor fleet.

The H-Cube® Pro is an all-in-one high pressure flow chemical synthetic platform that features on-demand hydrogen generation. The two built-in electrolytic cells generate up to 60 NmL/min H_2 gas at 100 bar pressure from Milli-Q water. The built-in gas-liquid mixer ensures a homogeneous distribution of H_2 in the liquid flow. The reactor part of the instrument can house 30 mm and 70 mm catalyst cartridges (CatCart®s) that can be cooled and heated from 10 °C to 150 °C. CatCart®s are pre-filled with many types of catalysts, eliminating user contact with catalyst materials. Custom catalyst testing is also available with the CatCart® Packer and Closer instruments. Designed with safety of utmost importance, the H-Cube® Pro features a multitude of automated safety features, including a built-in hydrogen sensor, overpressure protection and leakage detection.

DISCUSSION AND RESULTS

Highly efficient RAFT polymerization in a Phoenix Flow Reactor system[2]

Rigoberto Advincula's group used a Phoenix Flow Reactor equipped with an 8 mL stainless steel coil (1 mm ID), coupled with a Pressure Module for creating the desired pressures for continuous flow RAFT polymerization. The liquid was pumped through the system using an HPLC Pump (figure 1.). The researchers used a 1:1 mixture of EtOH/H_2O to purge the flow system at 2.00 mL/min flow rate for 8 minutes.

Following this the starting material consisting of the monomer Poly(ethylene glycol) methyl ethermethacrylate (PEGMEMA); RAFT-CTA (2-(((Butylthio)carbonothioyl)thio)propanoic acid); ACVA (thermal initiator) in EtOH/H_2O was pumped through the system at set flow rate, temperature and pressure.

Parameter optimization experiments revealed the effects of temperature, pressure, flow rate and concentrations: results show that at the same reaction temperature, RAFT polymerization can be performed at a higher efficiency in continuous flow compared to traditional batch methods.

This is due to continuous flow's higher thermal exchange efficiency.

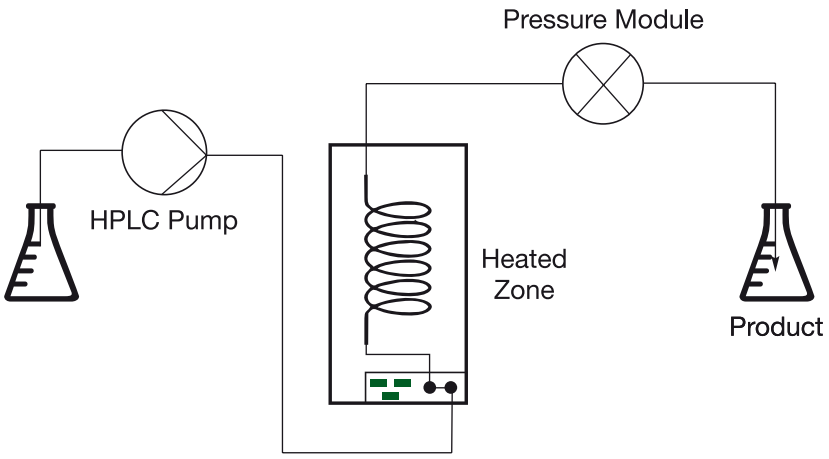

Figure 1: Schematic representation of the Phoenix II Flow Reactor platform used for RAFT polymerization

Operating at higher pressures prevents solvent overboiling, thus higher reaction temperatures can be used. Radical generation rate, propagation rate and chain transfer rate are all elevated using higher temperatures, leading to an increase in monomer conversion within a shorter residence time. Conversion and polymerization degree values were studied using ^{1}H NMR. Additionally, FTIR and Gel Permeation Chromatography were also caried out to fully characterise the product. All measurements and reaction optimization findings can be found in great detail in the original research article[2]. At 73 bar, 100 °C 16 minutes reaction time 41% monomer conversion was reached. Decreasing the liquid feed's flow rate to 0.3 mL/min (26.6 min residence time) increased the monomer conversion to 57%. Maintaining an acceptable molar mass dispersity while keeping the conversion close to the maximum, the optimal parameters for conversion (52%) and molar mass dispersity (D<1.25) turned out to be using 0.15 mmol/dm^3 monomer concentration at 100 °C and 73 bar with a residence time of 40 minutes (0.2 mL/min flow rate).

Temperature [°C]	Residence time [min]	Monomer conversion [%]	Mass dispersity
80	16	7	1.06
100	16	41	1.34
100	26.6	57	1.36
100	40	52	1.24

Table 1: Reaction parameters for RAFT polymerization[2]

Hydrogenation of end-functional polyisoprene and polymyrcene using the H-Cube® Pro[3]

Researchers in David M. Haddleton's team carried out end-functionalization of polyisoprene and polymyrcene using anionic polymerization and termination[3]. To induce the hydroxyl functional group in the final products, various epoxides were tried as terminating agents. Manipulation of all liquids were done under N_2 atmosphere in Schlenk tubes. The detailed process for the syntheses and analytics can be found in the original research article[3]. The functional polymers were subjected to ^{1}H and ^{13}C NMR, as well as MALDI-ToF MS and thermal analysis (TGA and DSC). The size distribution of samples was determined by Size-Exclusion Chromatography (SEC). Anionic polymerization allows for further functionalization, branching and linking reactions. Post polymerization modifications such as hydrogenation, thiol-ene reactions are highly useful to further improve polymer characteristics.

The researchers used an H-Cube® Pro equipped with 30 mm Pd/C CatCart®s for continuous flow hydrogenation of polymers (figure 2.). Functionalized polymyrcene (PMY) and polyisoprene (PIP) were dissolved in cyclohexane (0.1% w/V polymer/solvent). The reaction mixture was passed through the system at 0.5 mL/min flow rate at 70 bar pressure and 70 °C. ^{1}H NMR spectra confirmed >70% hydrogenation in the case of PMY with the retention of the end hydroxyl group. In the case of PIPs this value was >60% with retention of functional groups. Thermal analysis of the hydrogenated samples showed thermal stability increase in both PMY and PIP.

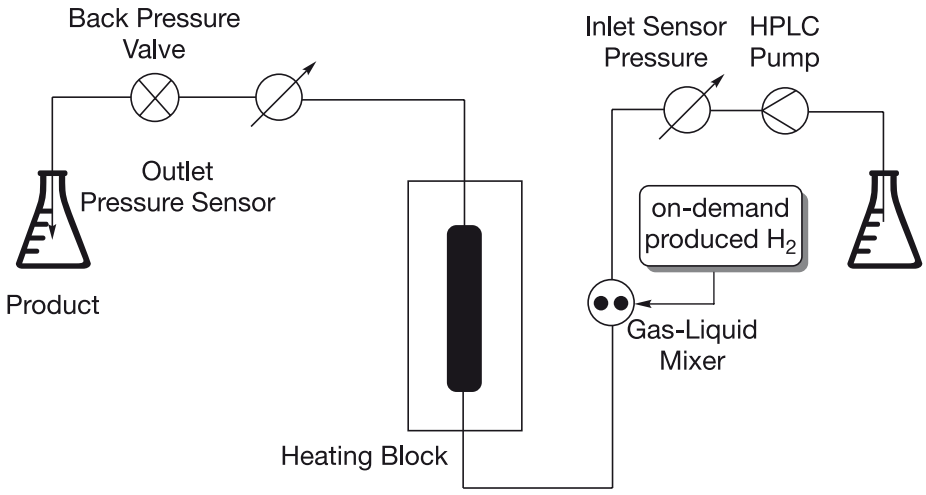

Figure 2: Schematic representation of the H-Cube® Pro system used for the hydrogenation of PMY and PIP

SUMMARY AND CONCLUSIONS

The Advincula Group's research paper sets a great example for the implementation of continuous flow techniques for RAFT polymerization. Using continuous flow, the highly efficient thermal transfer, high pressures and precise reaction control allowed for designing a scalable and predictable platform for synthesising polymers. The Haddleton Group's results show that continuous flow can not only be used in the polymerization process but also for post-polymerization modifications to further improve polymer characteristics.

REFERENCES

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