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Continuous Flow Synthesis of Terpene-Based Monomers for Green Polymers Production.

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Abstract

The synthesis of monomers for the production of novel green polymers was evaluated in continuous flow conditions using terpenes as dienes and maleic anhydride as dienophile for the [4+2] Diels-Alder cycloaddition reaction. The hydrogenation reaction was also evaluated to prevent the retro-Diels-Alder and to expand the reactional scope by producing adducts with distinct characteristics of structures and reactivity. Fourteen different monomers were obtained in good yields in flow regime.

Key words:

Flow chemistry, Diels-Alder, Terpenes

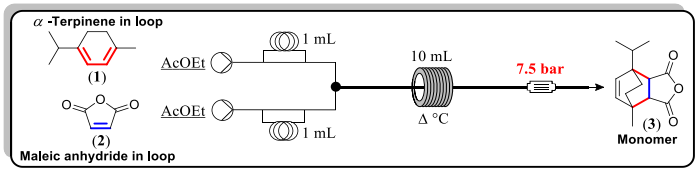
Introduction

Polymeric materials that incorporate renewable bio-based building blocks such as terpenes, provide a necessary alternative to our historical dependence on petroleum-based polymers. In that way, different terpenes such as *α*- and *β*-pinene, myrcene, phellandrene, limonene, terpinene have been applied to produce bio-based polymers.[1]

In this study, continuous flow processes were applied to the production of monomers for green polymer synthesis using terpenes as dienes and maleic anhydride as dienophile in a [4+2] Diels-Alder reaction.

Results and Discussion

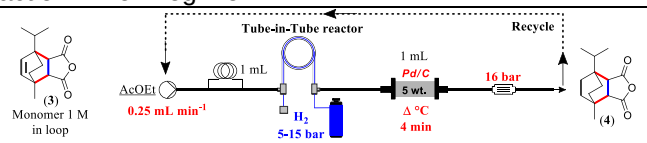
The synthesis of monomers started with the evaluation and optimization of the cycloaddition reaction using α-terpinene as diene (**scheme 1**), followed by the hydrogenation reaction (**table 1**).



Scheme 1: Diels-Alder reaction using α-terpinene as diene.

Total conversion (99%) was achieved using 0.25 mL min^{-1} at 140°C in 40 min.

Table 1: Heterogeneous catalysis for hydrogenation reaction in flow regime

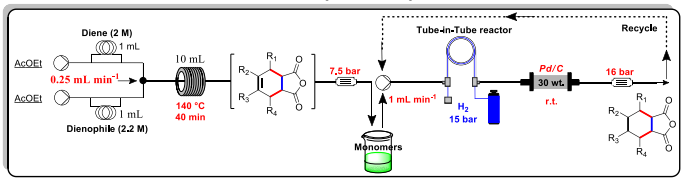


Entry	Temperature (°C)	Time (min)	H_2 (bar)	Conversion[b] (%)
1[c]	r.t.	4	5	2
2[c]	r.t.	4	10	5
3[c]	r.t.	4	15	10
4[c]	70	4	15	4
5[d]	r.t.	330	15	100

[a] Column details: Glass column with 750 mg of Pd/C (5% wt.) [b] Conversion was determined by GC-MS. [c] The reaction was conducted in a single-pass experiment. [d] It was recycled through the system.

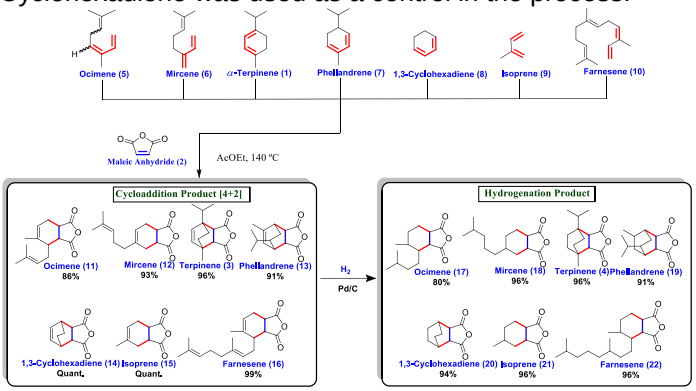
The **scheme 2** show the synthesis in two steps made in sequence on continuous flow using a tube-in-tube reactor.

For total conversion of monomer **3**, a recycle (entry **5**) was necessary and Pd/C 5% wt. was replaced by 30% wt. to decrease the reaction time (80 min).



Scheme 2: Sequential Diels-Alder reaction and heterogeneous hydrogenation in flow regime.

With these results, the scope was expanded using six different terpenes as shown in the **scheme 3.** 1,3-Cyclohexadiene was used as a control in the process.



Scheme 3: Scope using different terpenes as dienes.

Conclusions

The strategy adopted here allowed the synthesis of several monomers in good yields (up to 85%) and total conversion for terpenes in only 40 min for the Diels-Alder reaction. The flow process offers unique possibility to the scale-up of monomers synthesis without the need to increase the size of the coil reactor as it is requested in the batch process. Work is now in progress to produce novel bio-based polymers with these terpene-based monomers using polyols and polyamines as chain propagation agents.

Acknowledgement

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