doi:10.20396/revpibic262018898

XXVI Congresso de Iniciação Científica Unicamp
17 a 19 de outubro Campinas | Brasil

# 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*

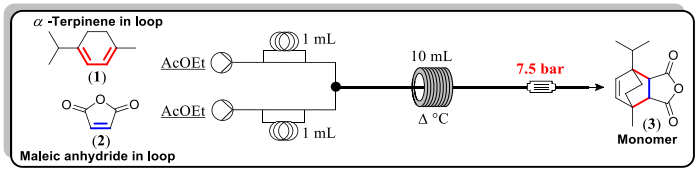
## Introduction

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

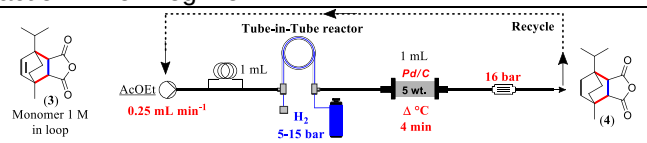
The synthesis of monomers started with the evaluation and optimization of the cycloaddition reaction using α-terpinene as diene (**scheme 1**), followed by the hydrogenation reaction (**table 1**).




**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

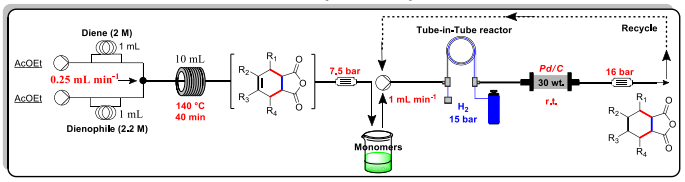



| Entry | Temperature (°C) | Time (min) | $H_2$ (bar) | Conversion[b] (%) |
|---|---|---|---|---|
| 1[c] | r.t. | 4 | 5 | 2 |
| 2[c] | r.t. | 4 | 10 | 5 |
| 3[c] | r.t. | 4 | 15 | 10 |
| 4[c] | 70 | 4 | 15 | 4 |
| 5[d] | r.t. | 330 | 15 | 100 |

[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.

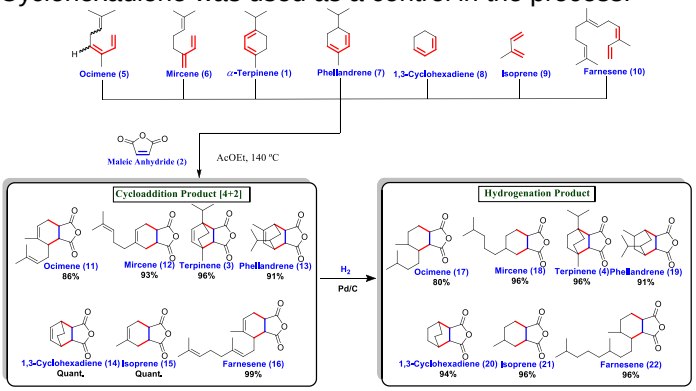
The **scheme 2** show the synthesis in two steps made in sequence on continuous flow using a tube-in-tube reactor.

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

The authors gratefully acknowledge financial support from FAPESP, CNPq CAPES and FAEPEX.

Perry, A. W.; Fuxiang, C.; Chuanbing, T. *Macromol. Rapid Commun*. **2013**, *34*, 8−37.