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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>H₂ (bar)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1[α]</td>
<td>r.t.</td>
<td>4</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>2[α]</td>
<td>r.t.</td>
<td>4</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>3[α]</td>
<td>r.t.</td>
<td>4</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>4[α]</td>
<td>70</td>
<td>4</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>5[α]</td>
<td>r.t.</td>
<td>300</td>
<td>15</td>
<td>100</td>
</tr>
</tbody>
</table>

[α]: Column details: Glass column with 750 mg of Pd/C (5% wt.) [β]: Conversion was determined by GC-MS. [γ]: The reaction was conducted in a single-pass experiment. [δ]: 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.

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