Stereoselective Polymerization and Copolymerization of Renewable (*E*)-4,8-Dimethyl-1,3,7-Nonatriene Using Titanium-Based OSSO Catalysts

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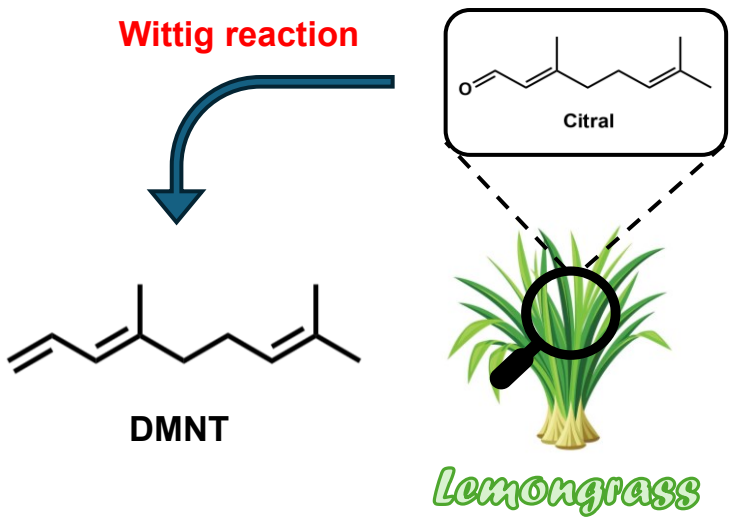
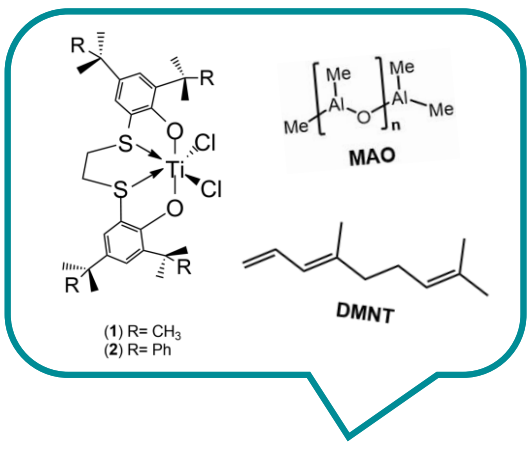
Introduction

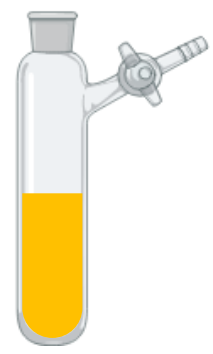
The environmental impact of petroleum-based plastics drives the search for sustainable alternatives from renewable sources. Bio-based polyolefins are promising due to their versatility and scalability. In this work, we explore the stereoselective polymerization of ***(E)-4,8-dimethyl-1,3,7-nonatriene (DMNT)***, a renewable monomer derived from citral, using titanium OSSO catalysts. These catalysts offer efficient, controlled polymerization and are based on earth-abundant, non-toxic titanium. The resulting polymers are highly isotactic, with elastomeric properties (Tg ≈ - 40 °C), suitable for flexible applications. We also investigated copolymerization with renewable monomers like *β*-myrcene, *β*-ocimene, 1-phenyl-1,3-butadiene (1PB) and *S*-4-isopropenyl-1-vinyl-1-cyclohexene (IVC) to tailor material properties. This study showcases titanium catalysis as a sustainable route to novel bio-based polyolefins.



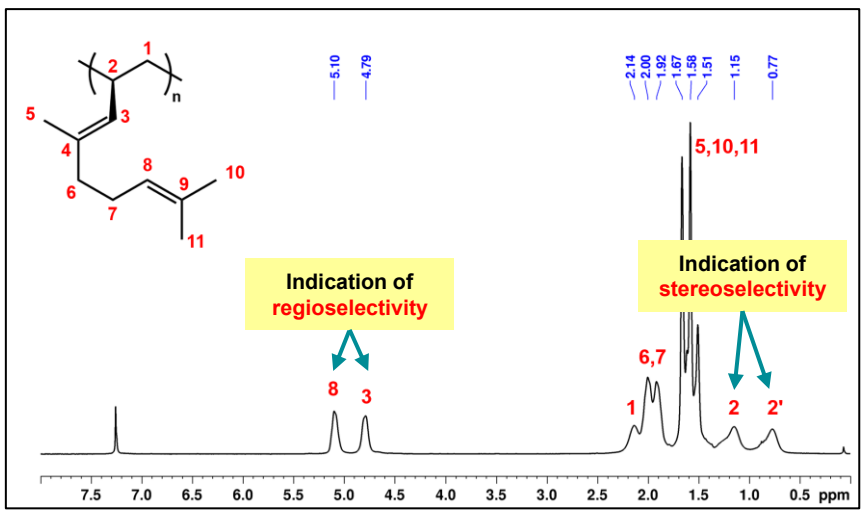
Stereoselective Polymerization of (*E*)-4,8-Dimethyl-1,3,7-Nonatriene

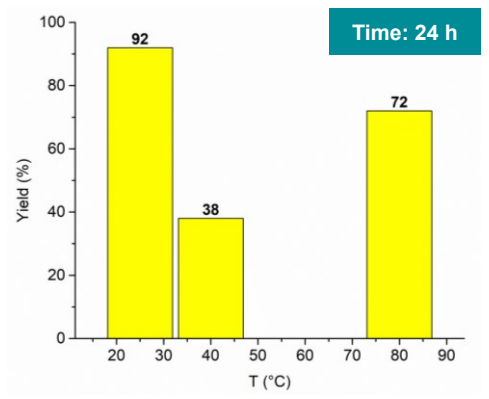


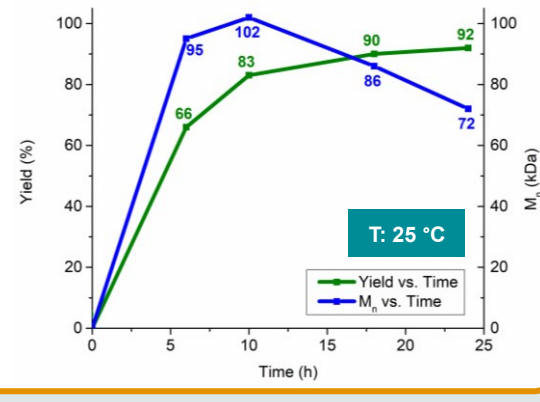
Reaction conditions:
Catalyst ($1.0 \cdot 10^{-5}$ mol)
[Al]/[Ti] = 500
DMNT (2 mmol, 0.3 g)
toluene (3 mL)



Both catalysts enabled predominant ***1,2-insertion*** of DMNT into the polymer chain. However, catalyst 2 demonstrated superior performance, yielding polymers with higher molecular weight. Its increased steric hindrance also led to enhanced control over the polymer microstructure, resulting in ***highly stereoregular*** materials (*mmmm* > 99%).



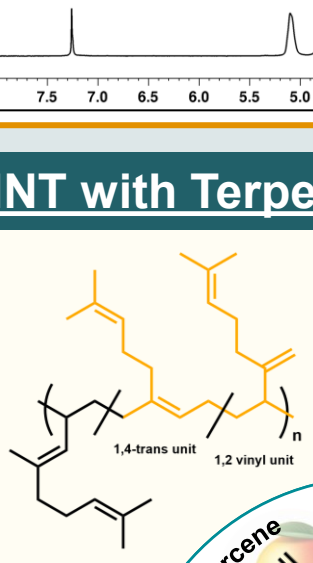


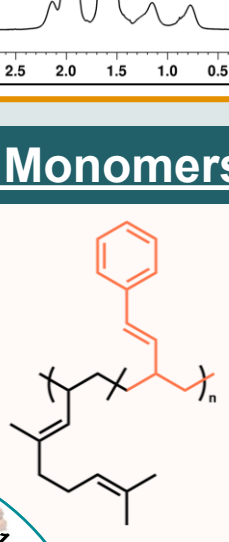


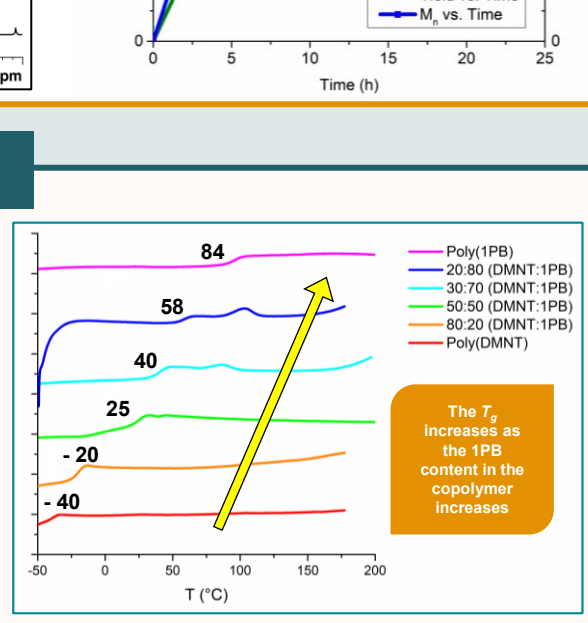
Copolymerizations of DMNT with Terpene-based Monomers

DMNT:M	T (°C)	Yield (%)	M_n (Kg/mol)	Đ	T_g (°C)
50:50	**25**	23	30.0	2.34	-42.6
50:50	**40**	44	19.2	2.07	-43.3
50:50	**80**	44	12.0	1.89	-46.3
80:20	80	74	16.6	2.05	-39.7
30:70	80	29	12.4	1.89	-51.8
20:80	80	24	12.3	1.85	-54.7

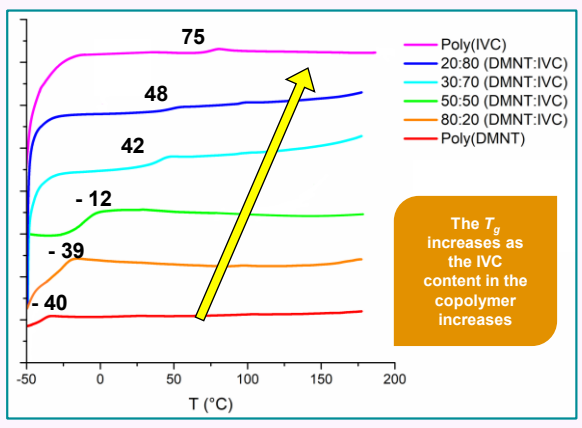
Reaction conditions: Catalyst ($5.0 \cdot 10^{-6}$ mol), ([DMNT]+[M])/[Ti] = 1000, [Al]/[Ti] = 500, toluene (5 mL), 24 h.



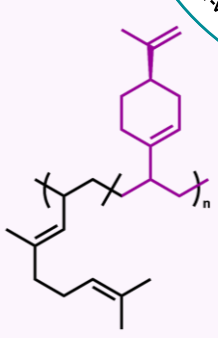




Reaction conditions: Catalyst ($5.0 \cdot 10^{-6}$ mol), ([DMNT]+[1PB])/[Ti] = 1000, [Al]/[Ti] = 500, toluene (5 mL), 40°C, 24 h.



Reaction conditions: Catalyst ($5.0 \cdot 10^{-6}$ mol), ([DMNT]+[IVC])/[Ti] = 1000, [Al]/[Ti] = 500, toluene (5 mL), 40°C, 24 h.



DMNT:O	T (°C)	Yield (%)	M_n (Kg/mol)	Đ	T_g (°C)
50:50	**80**	62	37.4	2.16	-33.6
80:20	80	78	43.0	2.39	-33.2
30:70	80	45	35.0	2.87	-31.5
20:80	80	63	31.1	2.39	-24.5

Reaction conditions: Catalyst ($5.0 \cdot 10^{-6}$ mol), ([DMNT]+[O])/[Ti] = 1000, [Al]/[Ti] = 500, toluene (5 mL), 24 h.

Conclusion

Isotactic, highly regioregular poly(DMNT) was obtained for the first time using titanium OSSO catalysts, demonstrating the efficiency and selectivity of this sustainable catalytic system. Copolymerization with rigid monomers such as 1PB and IVC enabled tuning of the glass transition temperature (T_g), with higher rigid monomer content leading to increased T_g values. In contrast, copolymers with β-myrcene and β-ocimene showed low T_g values (≈ -50 °C and ≈ -30 °C, respectively), yielding materials with elastomeric properties. These results highlight the versatility of titanium-based catalysis for producing tunable, bio-based polyolefins from renewable monomers.

References

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