

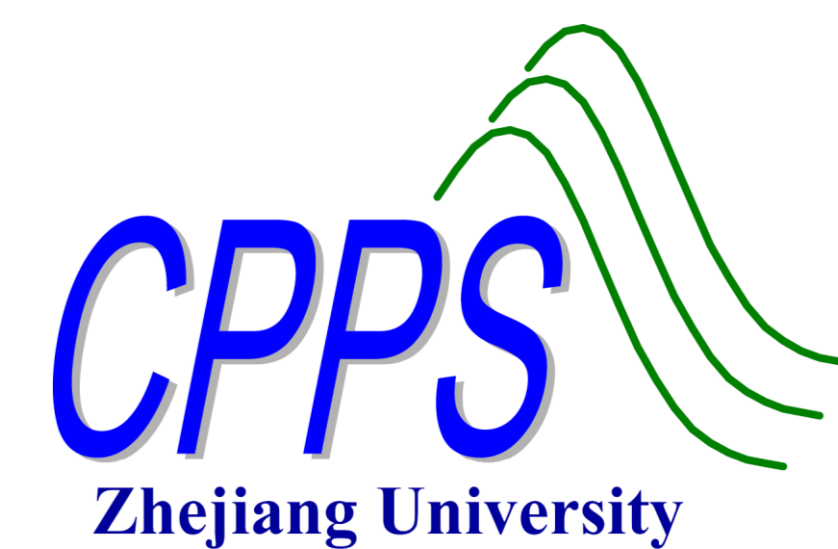
Tailor-made Low-branched Polypropylene Prepared by a Highly Active and Robust α -Diimine Nickel Catalyst



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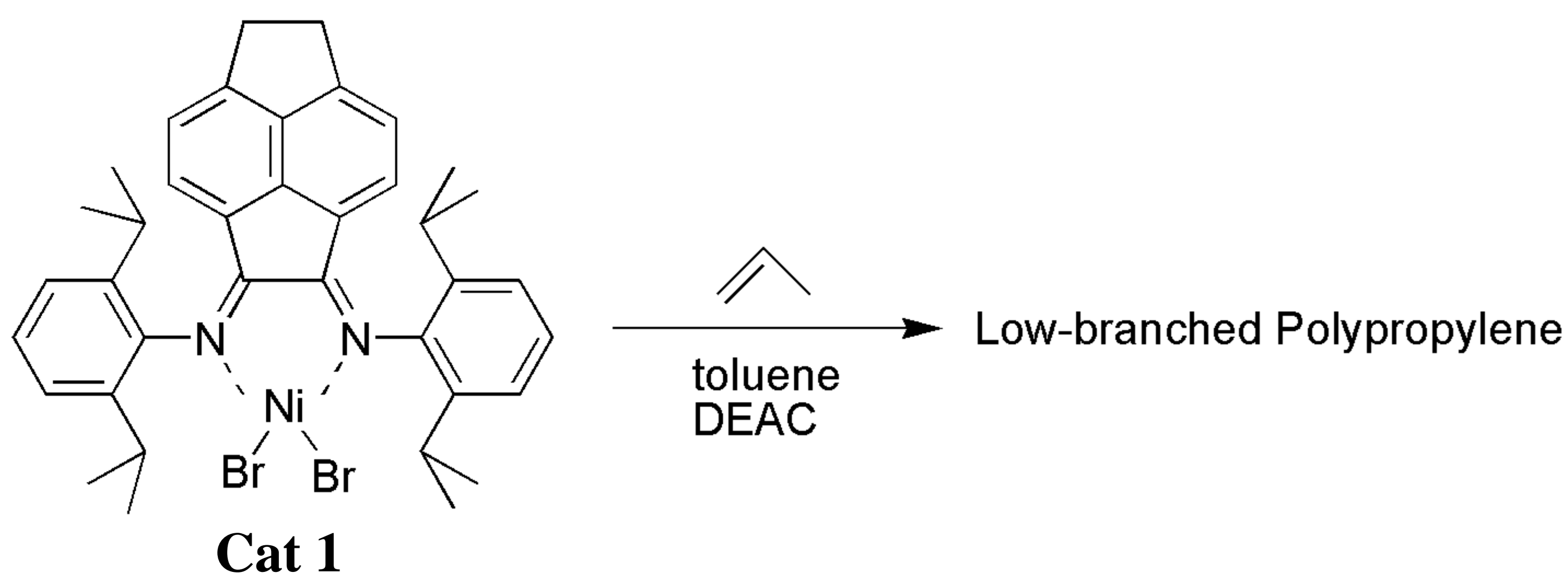
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Introduction

Living polymerizations allow for the synthesis of polymers with precisely controlled molecular weight, narrow molecular weight distribution, end-functionalized polymers, and well-defined block copolymers. Normally polypropylene (PP) is a thermoplastic polymer used in a wide variety of application. A new family of PPs has been synthesized by α -diimine nickel catalyst whose chain microstructures differ from PP produced by the early transition metal catalysts. So far there are only limited examples of living propylene polymerizations using α -diimine nickel catalyst. In this work, we present a new catalyst (Cat 1 in Scheme 1) belong to this camp and its performance under different kinds of polymerization conditions.

Experimental



Scheme 1. Route for preparing Low-branched Polypropylene by Cat 1/ AlEt_2Cl (DEAC).

Results and discussion

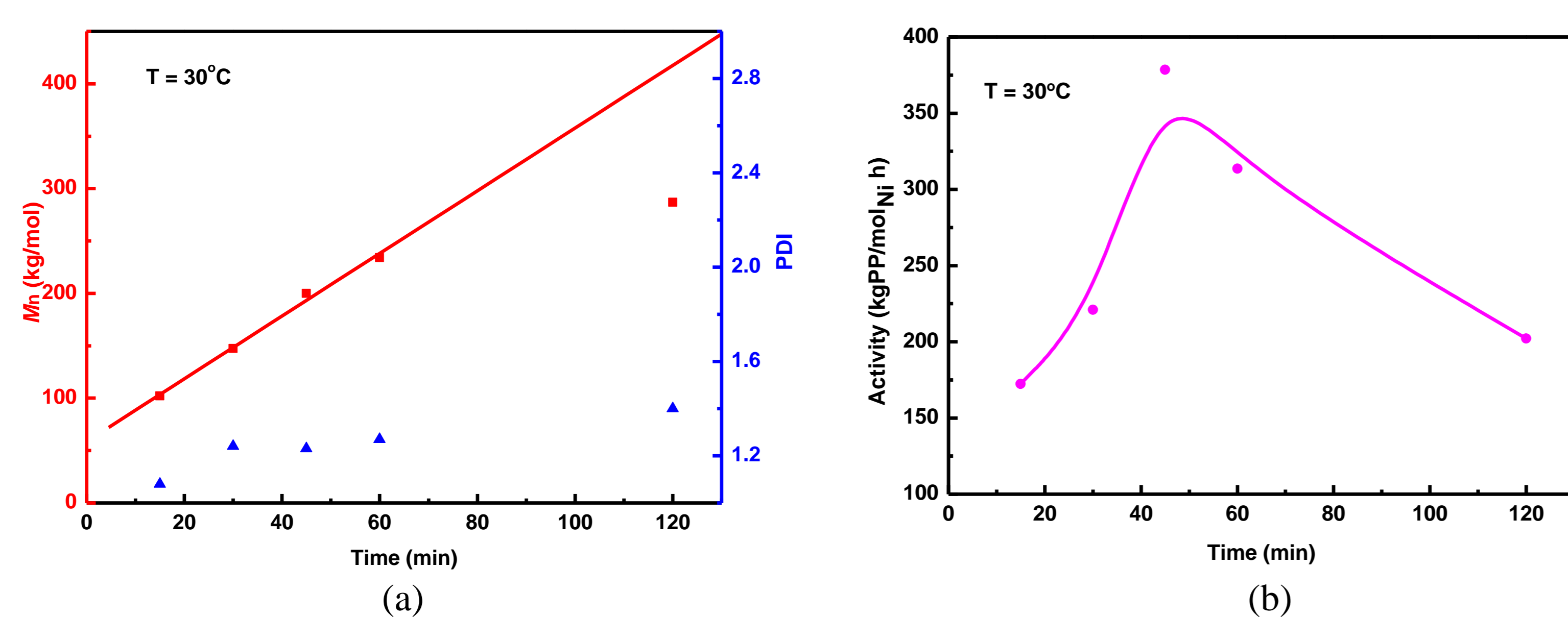


Fig 1. Plots of a: M_n (■) and PDI(▲) & b: Activity (●) as a function of polymerization time at 30°C under 1 atm of propylene using Cat1/ DEAC, Al/Ni=200, 50 ml toluene, [Ni] = 100 $\mu\text{mol/L}$.

PP M_n increases linearly with time over a broad molecular weight range while the PDI remains low (~1.2), indicating a living polymerization.

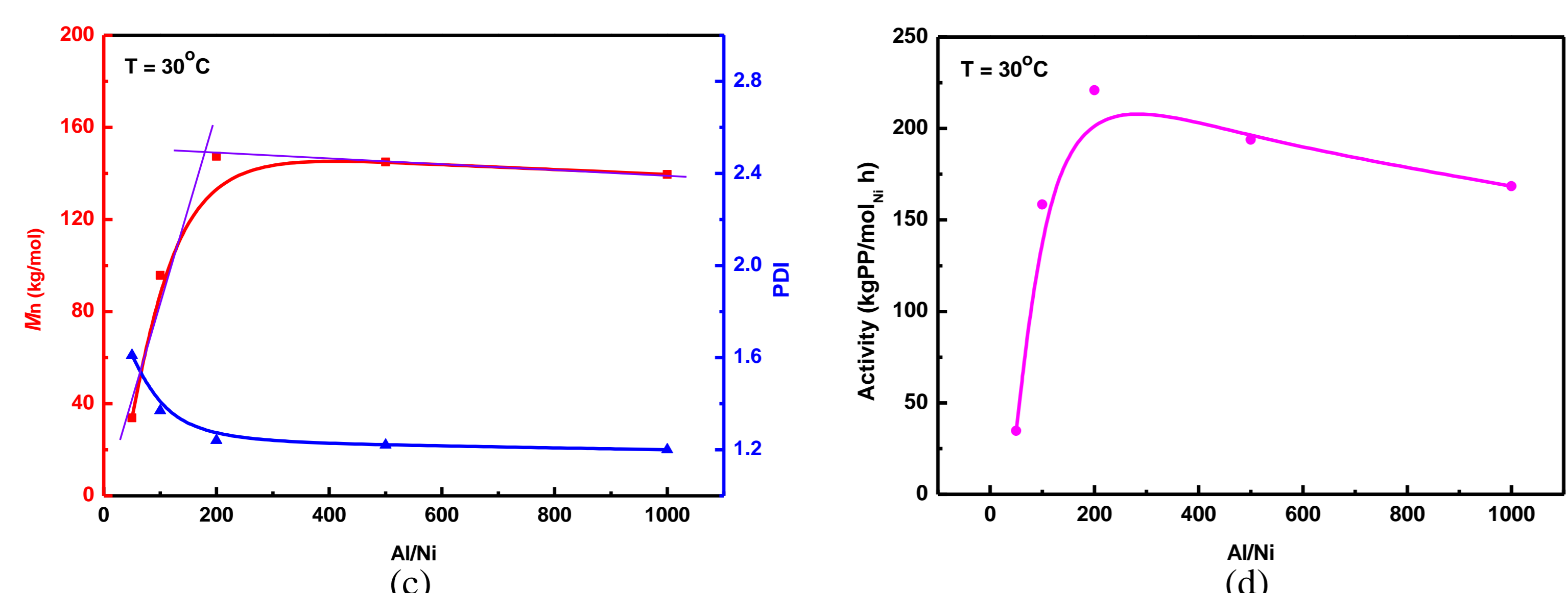


Fig 2. Plots of c: M_n (■) and PDI(▲) & d: Activity (●) of the PPs obtained at different Al/Ni ratio at 30°C under 1 atm of propylene using Cat1/ DEAC, 50 ml toluene, [Ni] = 100 $\mu\text{mol/L}$, Polymerization time = 30 min.

Proper Al/Ni ratio can activate and stabilize the nickel active center effectively, but higher Al/Ni ratio will lead to more chain transfer reaction.

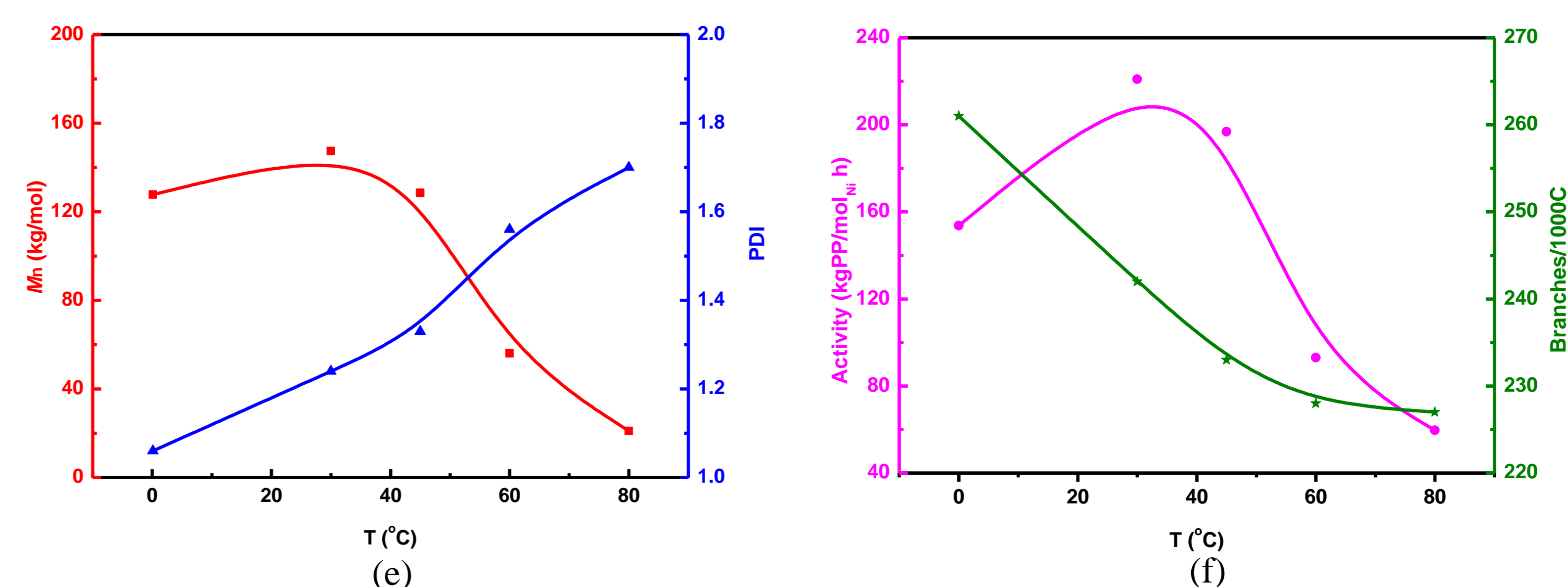
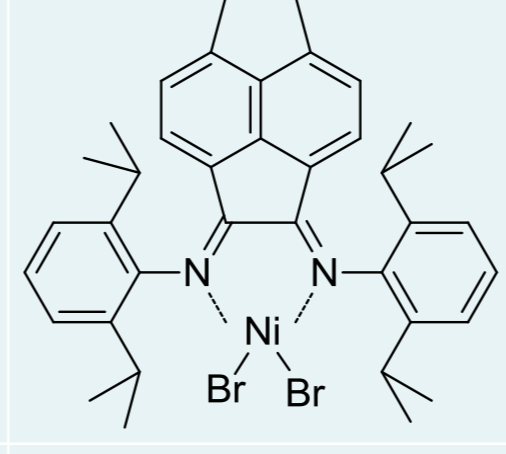
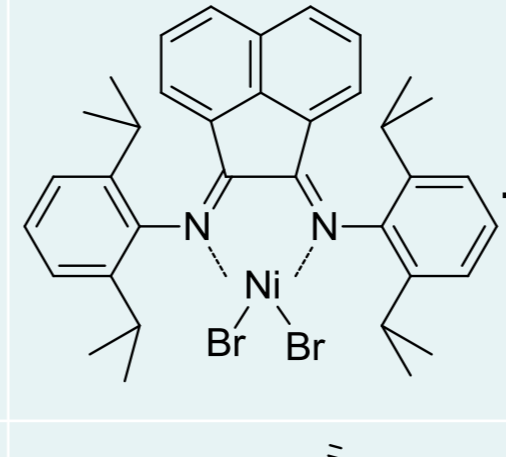
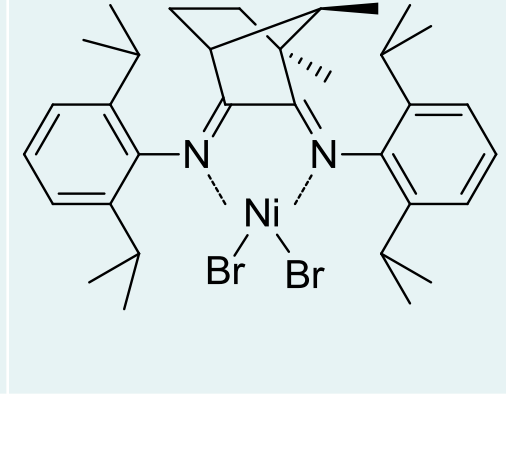


Fig 3. Plots of e: M_n (■) and PDI(▲) & f: Activity (●) and Branching degree (★) of the PPs obtained at different polymerization temperature under 1 atm of propylene using Cat1/ DEAC, 50 ml toluene, [Ni] = 100 $\mu\text{mol/L}$, Polymerization time = 30 min.

Low temperature will slow down the activation of the catalyst and restrict the chain walking due to the relatively high energy barrier. Elevate temperature will lead to more termination and chain transfer reaction.

Table 1. Rough comparison with similar reported catalysts by some run examples

Catalyst System	Temp (°C)	Time (min)	M_n (kg/mol)	PDI	Activity (kgPP/mol _{Ni} h)	Branches /1000C
1  +DEAC	0	30	128	1.06	154	261
	30	60	234	1.27	314	242
2  +MMAO	-10	60	160	1.13	105	297
	23	60	190	1.44	126	272
3  +DEAC	40	60	52	1.18	15	138
	70	60	33	1.31	14	126

Conclusions

In this poster, a tailor-made low-branched polypropylene was prepared by a new α -diimine nickel catalyst which has showed a very good polymerization activity and thermal stability. The influence of polymerization time, polymerization temperature and Al/Ni on polymerization activity, M_n , M_w/M_n and branching degree has been researched. In conclusion, propylene polymerization at 30°C (1 atm, 60 min) could yield PP ($M_n = 234 \times 10^3$) with $M_w/M_n = 1.27$ and the polymerization activity was as high as 314 kgPP/(mol_{Ni}·h). The functionalization and application of the low-branched polypropylene were being investigated in progress.

Acknowledgements

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References

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