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Coupling of ROMP/vinyl-addition by assisted tandem using Ru^{II}/Ni^{II} heterobimetallic complex

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The combination of two different metallic centers to the achieve a heterobimetallic system opens up opportunities for developing multifunctional catalysts, which can be used in tandem catalysis. Integrating two distinct mechanistic processes into a single protocol is particularly attractive in catalyst design. The coupling of the ring-opening metathesis polymerization and vinyl-addition polymerization (ROMP/vinyl-addition) by assisted tandem catalysis using Ru-Ni heterobimetallic complex and norbornene as monomer may be a versatile method for obtaining copolymers with new properties. In this sense, the heterobimetallic complex [{$RuCl_2(\eta^6$-*p*-cimene)}μ-(Schiff-pip)Ni(Aryl-NBE)(PPh_3)] (**Ru-Ni-NBE**) and [Ni(NBE-amide)(PPh_3)(Schiff-ciclohexane)] (**mono-Ni-Schiff**) were synthesized and fully characterized by spectroscopic and electrochemical techniques. **Mono-Ni-Schiff** and **Ru-Ni-NBE** were evaluated as pre-catalysts for the vinyl-addition polymerization of norbornene (NBE), achieving yields of 91 and 71%, respectively under optimized conditions using methylaluminoxane (MAO) as the cocatalyst. **Ru-Ni-NBE** was proved to be active also in ROMP of NBE, achieving up to 50% yield in the presence of 10 equiv. of (trimethylsilyl)diazomethane (TMSDM) as the carbene source. The one-pot synthesis of copolymer based on assisted-tandem catalysis ROMP and vinyl-addition polymerization of NBE using **Ru-Ni-NBE** was conducted via sequential addition of TMSDM and MAO under previously optimized conditions (Fig. 1). The copolymer was characterized by ^{1}H NMR, GPC, and Raman scattering.

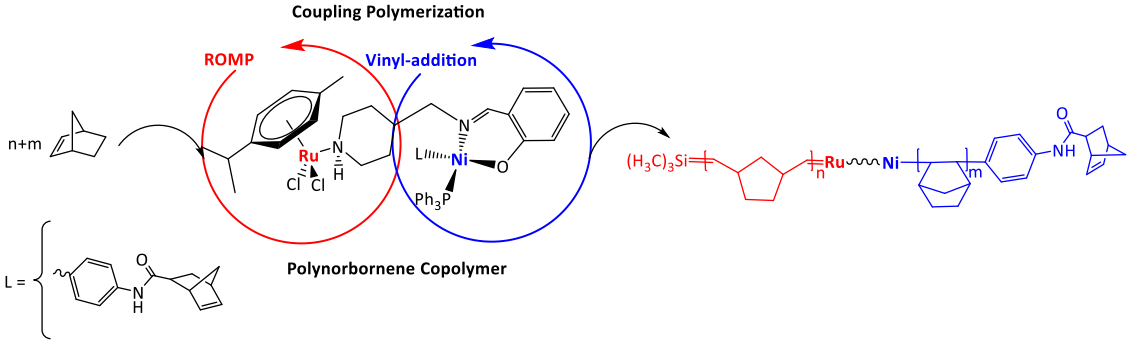

Fig. 1 Molecular structure of Ru-Ni-NBE and copolymer produced from the ROMP and vinyl-addition polymerization of NBE.

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References

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