

# Copolymers from norbornene and norbornadiene with organized morphologies and high $T_g$ values obtained via ROMP with highly reactive $[\text{RuCl}_3(\text{PCy}_3)_2]$ complex

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## Abstract

A metal-carbene species generated *in situ* from the starting  $[\text{RuCl}_3(\text{PCy}_3)_2]$  complex was able to polymerize *via* ROMP strained cyclic olefins very fast in non-degassed solution.

## Introduction

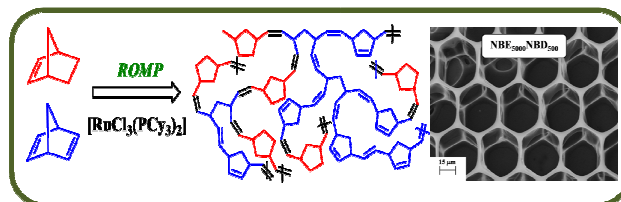
ROMP is catalyzed by a transition metal-carbene complex ( $\text{L}_n\text{M}=\text{CHR}$ ) through a metallocyclobutane intermediate produced from an intramolecular interaction between the metal-carbene moiety and the olefin. Usually, ancillary ligands in ROMP are bulky and good  $\sigma$ -donors.<sup>1</sup> Our motivation is to develop non-sensitive compounds to air, moisture, light and warmth, easily to be storage and that could match large practical applications in presence of molecular oxygen from air atmosphere.<sup>2</sup> The metal-carbene moiety has been generated *in situ* from reaction with a diazo compounds, contrary to the cases with pre-synthesized metal carbene complexes as the benzylidene complex types. Of course, an induction period precedes the ROMP initiation, and this step must be considered when interpreting the initiation and propagation steps in the ROMP reaction.

## Results and Discussion

The EPR spectrum of the paramagnetic  $[\text{RuCl}_3(\text{PCy}_3)_2]$  complex measured in the solid state (X band, 122 K) gave three signals. The  $g$  values are  $g_1 = 2.24$ ,  $g_2 = 2.05$  and  $g_3 = 1.89$ . This complex in a solution of  $\text{CHCl}_3$  with NBE and EDA (ethyl diazoacetate) shows a mixture of compounds. The formation of a diamagnetic species can be associated with redox processes via a disproportionation reaction ( $\text{Ru}^{\text{III}} \rightarrow \text{Ru}^{\text{II}} + \text{Ru}^{\text{IV}}$ ), but a high electronic density is required to obtain a high activity in ROMP reactions. Thus, we think that a main  $\text{Ru}^{\text{II}}$  complex is formed in presence of NBE and EDA, following the EPR spectra.

The SEM micrographs for the sample with  $[\text{NBE}]_{5000}[\text{NBD}]_{500}$  composition shows a highly

organized honeycomb-like pattern (Fig. 1). It is possible to obtain a regular pores in the presence of a cross-linking agent, but the regularity decreased on the copolymer morphology, as NBD load increased more than the double, and this can be associated with the higher reactivity of  $[\text{RuCl}_3(\text{PCy}_3)_2]$  with NBD. When the regularity decreased, the  $\tan \delta$  value increased (from 37 °C to 90 °C), once the mobility of polymer chains was affected by the porosity organization and by the cross-linking degree when increasing the NBD loads.



**Figure 1.** Illustration of copolymerization of NBE and NBD *via* ROMP and SEM micrographs for poly(NBE-*co*-NBD).

## Conclusion

$[\text{RuCl}_3(\text{PCy}_3)_2]$  complex presented high reactivity for ROMP of NBD and NBE. A high NBD content in poly[NBE-*co*-NBD] resulted in cross-linked polymers with noticeable improvement in the  $T_g$  values when compared with polyNBE. The micrographs revealed that the morphological shapes of the copolymers were sensitive to the NBD content, which can also be associated with the fast reaction with NBD.

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