Imido Vanadium(V)-Alkylidene Complexes for Olefin Metathesis Polymerization

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Olefin metathesis is a useful method applied for synthesis of various organic compounds (basic, fine chemicals, pharmaceuticals etc.) and polymers, advanced materials. It has been known that metal-carbene (alkylidene) complexes play a key role in this catalysis [1]. Study on synthesis and reaction chemistry of vanadium-alkylidene complexes also has been considered as an attractive subject [2], due to their potentials in catalysis displayed by classical Ziegler type vanadium catalyst systems in olefin polymerization and importance in organometallic chemistry [2].

We reported that (imido)vanadium(V)-alkylidene complexes containing anionic donor ligands exhibited catalytic activities for ring-opening metathesis polymerization (ROMP) of norbornene (NBE), and the derivatives [2c,3]. Since the activity is affected by the ligand set employed, we thus herein introduce synthesis of a series of (arylimido)-vanadium(V)-alkylidene complexes containing halogenated alkoxo/aryloxo ligands (**1**-**5**) and their potentials as catalysts for ROMP of cyclic olefins [3,4].

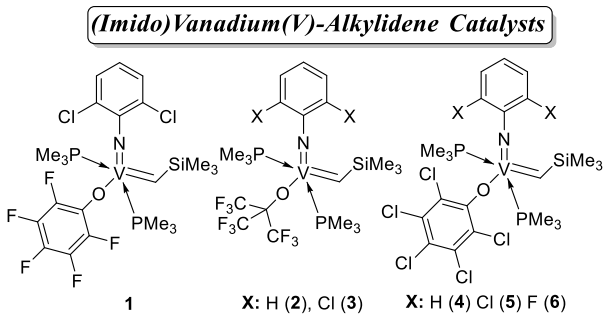
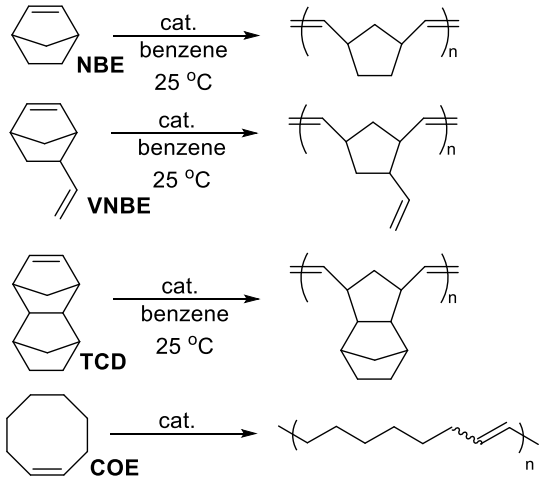


Chart 1. (Imido)vanadium(V)-alkylidene complexes for ring-opening metathesis polymerization (ROMP) of cyclic olefins.

It turned out that these catalysts displayed remarkable activities and the resultant polymers possessed ultrahigh molecular weights with narrow molecular weight distributions, suggesting a possibility of living polymerization. Aryloxo analogues showed rather higher activities than the alkoxo analogues, although the activity was also affected by the nature of imido ligand.

Note that efficient *cis*-specific ROMPs have also been achieved by using the alkoxo analogues (**2**,**3**), and the high *cis* selectivity (>98 %) could be maintained even at high temperature (80 ºC).

Importantly, ROMP of cyclooctene (COE) by **5** took place and the activity increased at high temperature affording rather high molecular weight polymers with uniform molecular weight distributions. More details will be introduced in the symposium.



Scheme 1. ROMP of cyclic olefins.

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