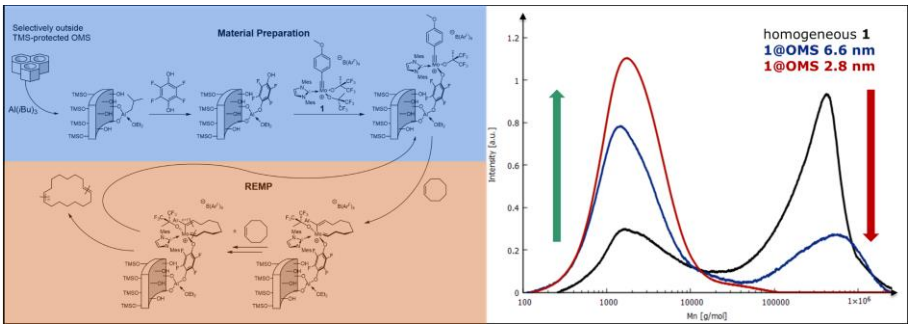
Ring-Expansion Metathesis Polymerization of Cycloolefins by Cationic Mo Alkylidyne NHC Complexes in Confined Geometries

Patrick Probst[1], Dongren Wang[1], Michael R. Buchmeiser[1]

[1]Institute of Polymer Chemistry University of Stuttgart, Pfaffenwaldring 55, D-70569 Germany

E-Mail presenting author: patrick.probst@ipoc.uni-stuttgart.de

Cationic Mo alkylidyne *N*-heterocyclic carbene (NHC) complexes, e.g. [Mo(C-p-C_6H_4OMe)($OCMe(CF_3)_2)_2$)(1,3-dimesitylimidazol-2-ylidene)$^+$][$B(Ar^F)_4^-$] (**1**),[1] were investigated towards their ability to catalyze the ring-expansion metathesis polymerization (REMP) of cyclic olefins.[2] Complex **1** was successfully immobilized on ordered mesoporous silica (OMS) of which the outer surface was passivated by trimethylsilane (TMS) groups. Two materials with pores 6.6 nm and 2.8 nm in diameter were prepared. Under these conditions, the complex initiates REMP of *cis*-cyclooctene (*c*COE) (Scheme 1, left) to form poly(*c*COE). A confinement effect in its formation was observed by size exclusion chromatography (SEC). While the homogeneous catalyst **1** mainly forms high molecular weight polymers ($\overline{M_n}$=183.000 g/mol), immobilization of **1** inside the pores of 2.8 nm OMS suppresses the formation of the high molecular weight fraction and only low molecular weight oligomers form ($\overline{M_n}$ =1.400 g/mol, Scheme 1, right). Details on the preparation of nonporous reference materials to differentiate between surface and confinement effects as well as on the REMP of *endo,exo*-2,3-dicarbomethoxynorborn-5-ene will be outlined.



Scheme 1: Catalyst immobilization on OMS selectively protected with TMS outside, followed by REMP of *c*COE (left). SEC of poly(*c*COE) prepared by **1** immobilized on different silica materials (0.25 M, C_6D_6, 80 °C, 16 h, cat:monomer = 1:1000, right).

[1] J. Groos *et al.*, Organometallics, 2021, **40**, 1178, doi: 10.1021/acs.organomet.1c00175
[2] P. Probst *et al.*, J. Am. Chem. Soc., 2024, **146**, 8435, doi: 10.1021/jacs.3c14457