Latent Olefin Metathesis Catalysts for Polymerization of Dcpd

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Summary: Advances in design of latent ruthenium phenylindenylidene catalysts bearing salicylaldimine ligands for ring-opening metathesis polymerization are described. The presence of the substituents in ortho position in N-aryl ring of salicylaldimine ligand has been found to be the main factor determining the catalyst stability. The best of the studied catalysts after acid activation offers activity comparable to that of the dichloride systems in ring-opening metathesis polymerization of DCPD, while maintaining very high stability in the monomer solution.

Keywords: latent catalysts; ring opening metathesis polymerization (ROMP); poly(dicyclopentadiene)

Introduction

The formation of carbon-carbon bonds by olefin metathesis has become one of the most powerful synthetic tools of chemists mainly due to its versatility and the development of well-defined catalysts stable to demanding reaction conditions [1] A major breakthrough in the olefin metathesis development was established by the discovery of the ruthenium complexes bearing N-heterocyclic carbene ligand **1** (Scheme 1).

The particular examples of NHC bearing catalyst are so called latent catalysts exhibiting low initiation rate, which are of particular interest in ROMP reactions in which the long handling of catalyst monomer solution is required.[2]

Schiff base containing catalysts reported by Verpoort et al. were shown to be extremely inactive at room temperature towards the polymerization of cyclic olefins such as DCPD and have to be activated by the addition of Bronsted acids, e.g. HCl.[3]. Such behaviour of the catalysts could be of interest in a Reaction Injection Moulding process where the catalyst can be stored together with the monomer while a second monomer stream contains acid to activate the catalyst.

Driven by the challenge to find sufficient latent catalyst for DCPD polymerization and better synthetic strategies to avoid the quite cumbersome preparative routes via diazo compounds, we attempt to explore the salicylaldimine complexes containing phenylindenylidene ligands. In this case the introduction of the alkylidene moiety undergoes in the mild conditions by using non hazardous commercially available compounds.[4]

Latency Study

The catalysts latency is of major importance for ROMP of DCPD, where it allows for mixing of monomer and catalyst without concomitant gelation or microencapsulation. As shown in Table 1, catalysts **3a-f** (Scheme 2), were subjected to selected latency and stability tests to gain some idea on their pot life in comparison to the reference catalysts **1** and **2**. Entry 1- 4 (Table 1) illustrates the high stability of the

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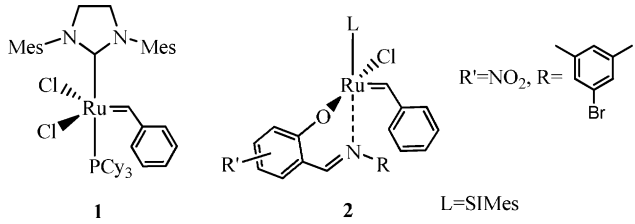


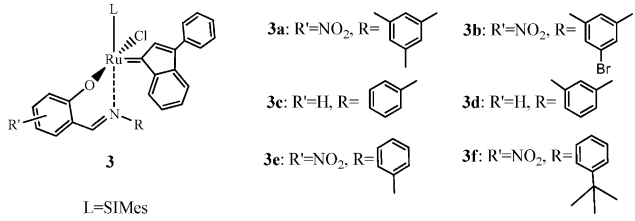
Scheme 1.
Well defined ruthenium metathesis catalysts.

phenylindenylidene Schiff base complexes **3a-d** in DCPD monomer. During a time period of 7 days, no degree of viscosity increase was observed. In contrast to the complexes **3a-b**, the catalysts **3e-f** (Entry 5 and 6) are sufficiently more active to allow slow polymerization of the monomer (Table 1). A dissociative mechanism in which catalyst initiation level depends upon neutral ligand dissociation is the most reliable for the olefin metathesis reactions catalyzed by Grubbs complex **1** and it also holds for indenylidene Schiff base complexes. The activation of the salicylaldimine pre-catalysts via nitrogen ligand decoordination can be expected to be a function of the sterical hindrance and charge distribution in these complexes. The withdrawing character of nitro group in salicylaldimine ligand in **3a-b** makes the Ru center more electophillic, in conjunction with the greater sterical hindrance, accounts for the lower lability of nitrogen ligand, and consequently the low initiation efficiency of these complexes. Despite the presence of nitro group in phenoxy moiety the catalyst **3e-f** show distinctly lower stability compared to **3a-b.** The difference in the stability of the catalysts **3a-b** and **3e-f** can be rationalized only in terms of the influence of steric effects of the substituents in N-aryl group on the initiation rate. On the basis of the observed stability trends one may assume, that the steric encumbrance of the bulky ligands, namely the presence of at least one substituent in ortho position to the nitrogen atom is the main factor determining the stability of the complexes **3a-d** in DCPD monomer. Furthermore the good stability of the catalysts **3c** bearing salicylaldimine ligand with one methyl group in *ortho* position to nitrogen ligand is in a good agreement with this reasoning.

Table 1.
Latency of catalysts **2**, **3a-f** in DCPD (at room temperature).

Entry	Catalyst type	Viscosity before storage Cps	Viscosity after storage Cps
1	**3a**	10	10
2	**3b**	10	10
3	**3c**	10	10
4	**3d**	10	10
5	**3e**	10	2365
6	**3f**	10	Solid
7	**2**	10	10

The catalysts/DCPD ratio= 1/15000, time = 7 days, temperature = 20 °C.



Scheme 2.
Ruthenium phenylindenylidene catalysts bearing salicylaldimine ligands **3a-c**.

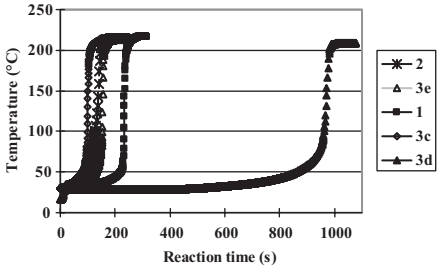


Figure 1.
The activity of the catalysts **3c-e**, **2**, **1** in solvent free ROMP of DCPD at 30 °C.

Catalyst Performance

Complexes **3a-f, 1 and 2** were tested for ROMP of DCPD. The low lability of the nitrogen ligand at room temperature is implied by the requirement for the chemical activation in order to achieve high activity, as it has been earlier found for Schiff base catalysts **2.**[5] The catalysts **3a-b** upon acid activation did not show activity at 30 °C. Steric effects in combination with higher electophilicity of ruthenium centre can thus be so strong to alter completely the activity of complexes **3a-b** at room temperature. Introduction of the ligand without electron withdrawing group resulted in the complex **3d**, which shows enhanced activity at room temperature after acid activation (Figure 1). The logical approach to further improvement of the catalyst activity was achieved by introduction of the less sterically demanding salicylaldimine ligand with only one methyl group in ortho position in N-aryl ring (Scheme 2, catalyst **3c**). Results (Fig. 1) fully illustrate that, for all tested catalyst **3c** enables DCPD polymerization at short reaction times (100 seconds.), by far superior to this attained by dimethylphenyl derivative **3d** as well as other ruthenium indenylidene salicylaldimine catalysts and the reference catalysts **1** and **2**.

The catalysts **3c-f** and **2** are chemically activated by 45 equivalents of *in situ* generated HCl.

The catalysts feature of prominent importance for DCPD polymerization is on one hand decreased initiation rate, which allows for mixing of monomer and catalyst but also stability against the decomposition during the long-term storage in monomer. Table 2 shows the activity of precatalyst **3a-d, 2** activated by *in situ* generated hydrochloric acid relative to the activity of the same catalysts stored for seven days in DCPD at a monomer/catalyst ratio of 15,000/1. The Schiff base ruthenium catalysts **3a-d** and **2** display high stability even upon storage for several days, in DCPD monomer, hence almost no change in reactivity after chemical activation has been observed. These combined high catalyst stability, impressive robustness against the decomposition and high activity upon chemical activation is a unique feature among olefin metathesis catalysts.

Conclusions

The foregoing describes a latency, stability and catalytical activity study of Ru indenylidene complexes containing salicylaldimine ligands in ROMP of DCPD. It has been proved, that only catalysts containing salicylaldimine ligands with the sterical hindrance in N-aryl ring (**3a-d)** show excellent stability in DCPD monomer. The

Table 2.
Performance of the catalyst **3a-d**, and **2** before and after storage in DCPD (at room temperature)[a].

Catalyst	Initial reaction time[b]	T_{max}	Reaction time after storage[b]	T_{max}
3a	no reaction	–	no reaction	–
3b	no reaction		no reaction	–
3c	100	212	98	212
3d	582	209	579	210
2	128	215	134	215

[a]Conditions: DCPD/Ru= 15000/1, time = 7 days, under air, room temperature.
[b]tests at 30 °C.

catalyst **3c** appeared to be the most attractive for ROMP of DCPD combining the high performance after acid activation with excellent stability in the monomer solution.

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