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Multi-nuclear dendritic Ru-complexes as catalysts for ROMP; synthesis and characterization of starpolymers

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Abstract

Multi-nuclear dendritic Ru-complexes were used as a core molecules in the "core-first" synthesis of star-shaped polynorbornene. The activity and selectivity of the dendritic catalytic systems have been evaluated. In addition the influence of the dendritic catalyst on the molar mass and molar mass distributions of the starpolymers has been studied. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

During recent years, olefin metathesis catalysts have gained a position of increasing significance owing to their versatile applications in organic and polymer syntheses [1]. The rapid progress in recent years has been triggered off by the discovery of the Grubbs catalysts in mid 1990s [2–5]. It has been demonstrated that the single-component alkylidene ruthenium complexes, $Ru(=CHPh)(PR_3)_2$ (R = Ph (**1**), Cy (**4**)) exhibit high catalytic activity and excellent tolerance towards polar functional groups. Their pioneering work was followed by many other studies which described the 'fine-tuning' of Grubbs' system.

In a recent paper, we reported a preliminary study on the combination of a Grubbs catalyst with low generation dendrimers [6]. Carbosilane (CS) dendrimers

were selected as supports since their inertness allows the use of a range of organometallic reagents in synthetic procedures. Due to the well-defined functionalized structure of these dendrimers, the attachment of the Ru-complexes could be performed in a controlled manner. This resulted in the formation of a well-defined number of catalytic-sites on the surface of the CS dendrimer which are easily accessible for the substrates. These dendritic Ru-complexes were shown to be efficient catalysts for the ring-opening metathesis polymerization (ROMP) of norbornene (nbe) [6]. In our concept the Ru-complexes are connected to the dendrimers by the carbene function and the star-shaped dendritic core molecules determine the final structure of the polymer. As a result the polymers are star-shaped. This route is advantageous compared to other methods for the formation of starpolymers, since the number of branches is pre-defined by the dendritic core [7].

In this article, we present the results of a detailed study on the catalytic activity and selectivity of

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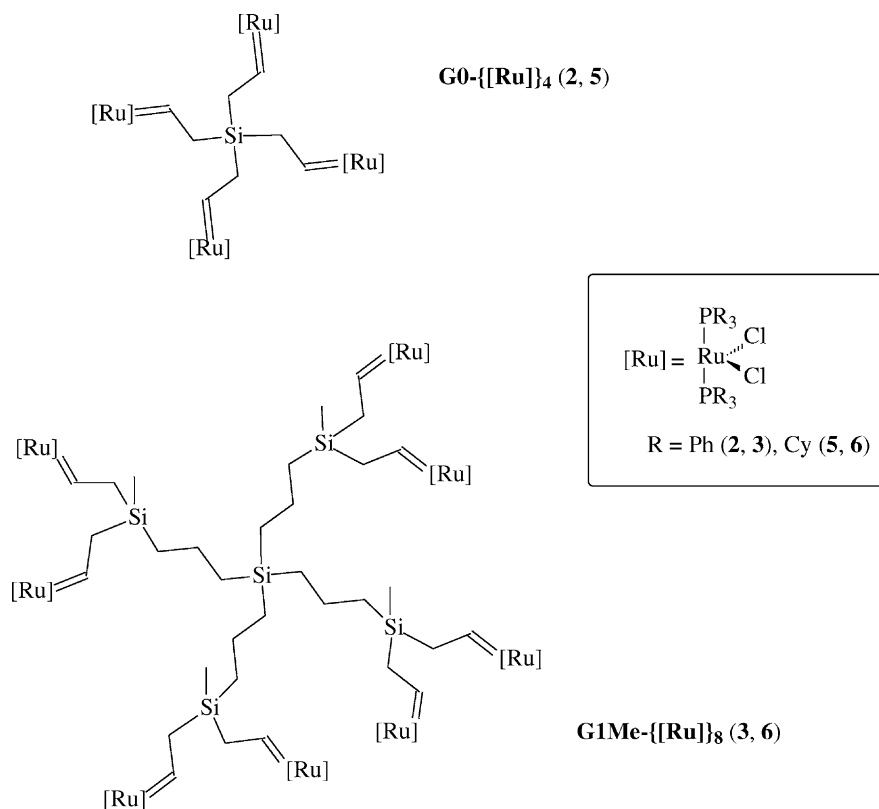*E-mail address:* francis.verpoort@rug.ac.be (F. Verpoort).

Fig. 1. Dendritic Ru-catalysts.

different dendritic Ru-systems as ROMP catalysts (Fig. 1). We also disclose a detailed study of the characterization of the star polynorbornene.

2. Experimental

2.1. General

All experiments were performed under purified inert gas using Schlenck techniques. Commercial grade solvents were dried and deoxygenated for at least 24 h over appropriate drying agents under nitrogen atmosphere and freshly distilled prior to use. ^{1}H-NMR spectra were recorded at 500 MHz and 25 °C on a Brucker AM spectrometer. Infrared spectra were performed on a Mattson 5020. GPC spectra were recorded in CHCl$_3$ using a 5 μm PL-gel Mix-kolom (60 cm, $d = 7.5$ mm). A Waters 401 RI-detector is used and

the flow is 1 ml/min (concentration = 2%). Calibration is done by means of polystyrene standards.

The syntheses of the catalysts were carried out as reported previously [6].

2.2. Polymerization procedure

To 4 mmol norbornene in dry dichloromethane (11 ml, 0.36 M), a solution of the G1-{[Ru]-PPh$_3$}$_8$-catalyst (3, 31 mg, 5 μmol) in dry dichloromethane is added under nitrogen atmosphere. After stirring the solution at room temperature for 60 min, a solution of CH$_2$Cl$_2$ (5 ml), 2,6-di-*t*-butyl-4methylfenol (0.2 g) and ethylvinylether (2 ml) is added in order to terminate the polymerization. The solution is stirred at room temperature till deactivation of the active species is completed. After filtration through a short celite-column the polymers were precipitated by pouring the mixture into methanol. The polymers

Table 1

Concentrations of the different Ru-catalysts for the polymerization of nbe

Catalyst	[Catalyst] (mol/l)	[Catalytic-sites] (mol/l)
Mononuclear systems (**1** and **4**)	2.5×10^{-3}	2.5×10^{-3}
G0-systems (**2** and **5**)	6.25×10^{-4}	2.5×10^{-3}
G1Me-systems (**3** and **6**)	3.13×10^{-4}	2.5×10^{-3}

Table 2

Conversion of the polymerization reactions with the different catalytic systems (**1–6**)

Catalyst	Maximum conversion (%)[a]	TOF/Ru[b]
$Ru(PPh_3)_2Cl_2(=CHPh)$ (**1**)	97	1.62
$Ru(PPh_3)_2Cl_2(=CHPh)$ + G0 (**2**)	96	1.60
$Ru(PPh_3)_2Cl_2(=CHPh)$ + G1Me (**3**)	92	1.53
$Ru(PCy_3)_2Cl_2(=CHPh)$ (**4**)	98	6.53
$Ru(PCy_3)_2Cl_2(=CHPh)$ + G0 (**5**)	98	6.53
$Ru(PCy_3)_2Cl_2(=CHPh)$ + G1Me (**6**)	97	6.47

Reaction conditions: CH_2Cl_2, 25 °C, catalyst/monomer = 1/100 (per Ru-complex), [Ru-sites] = 2.5×10^{-3} M.

[a] 60 min: **1–3**; 15 min: **4–6**.

[b] Average TOF (per minute, per ruthenium) based on the maximum conversion time.

were washed with methanol and dried in vacuum overnight.

In the polymerization experiments, the concentration of the metallodendrimer is varied, in order to obtain a constant concentration of the actual catalytic-sites (Table 1). The conversions of the different polymerizations were determined gravimetrically. In all experiments the ratio Ru/monomer is constant (1/100).

3. Results and discussion

We have previously reported the dendritic catalysts which can be synthesized by a simple olefin metathesis reaction between the Grubbs catalysts and the dendrimers [6]. These tetra- and octa-functional Ru-complexes (Fig. 1, compounds **2**, **3**, **5** and **6**) were used as dendritic catalyst for the polymerization of norbornene. In the activity study, the average TOF (turn over frequency per ruthenium centre) is used to compare the dendritic systems to the mononuclear analogues (Table 2). For the dendritic Ru-complexes the average TOF/Ru is comparable with the average TOF/Ru of the corresponding mononuclear complexes [8]. The good accessibility of the active catalytic-sites for the incoming monomer molecules is demonstrated. Furthermore, no synergetic effects between the Ru-catalyst and the dendritic matrix are observed.

For the catalysts resulting from the combination of the PPh$_3$-based Ru-complexes with the dendrimers, a difference in polymerization rate is observed (Fig. 2). The mononuclear Ru-complex **1** has the highest polymerization rate, followed by the G0 and G1 dendrimer. The dendritic multi-nuclear Ru(PCy$_3$)-catalysts (**5** and **6**) show a similar activity per metal centre in the ROMP of norbornene when compared to the

corresponding mononuclear analogue (**4**). After 15 min the conversion is nearly quantitative for the cyclohexyl based systems (**4–6**), while for the phenyl-systems a reaction time of 1 h is necessary to obtain the maximum conversion level. The increased donor-capacity, in combination with the larger cone-angle of the cyclohexylphosphines is responsible for this fact. This trend is also observed for the dendritic systems which can be explained by the fact that the phosphine ligands are not affected by anchoring the Ru-complexes to the dendrimer surface.

In addition to the activity, the influence of the dendritic catalysts on the stereoselectivity is studied. ^{1}H-NMR and IR-analysis indicate that the unsaturation in the polymers is retained, which is an indication for the ring-opening metathesis mechanism. In the IR-spectrum the high amount of *trans* double bonds is confirmed by the stronger absorption of the *trans* =CH out-of-plane bending at 966 cm^{-1} compared with the absorption at 1445 cm^{-1} for the *cis* =CH in-plane bending. The stereochemistry of the double bonds in the resulting polymers has been determined by ^{1}H-NMR. The ^{1}H-spectrum shows the characteristic doublets of doublets for the *trans* and *cis* olefinic protons. Previous studies with this type of Ru-catalysts indicated that mainly *trans* double bonds were formed in the polymerization of norbornene. For the dendritic systems, the amount of *trans* double bonds is between 82 and 89%, which is in accordance with the *cis/trans* ratio obtained with the free complexes (**1** and **4**). No appreciable difference in selectivity is
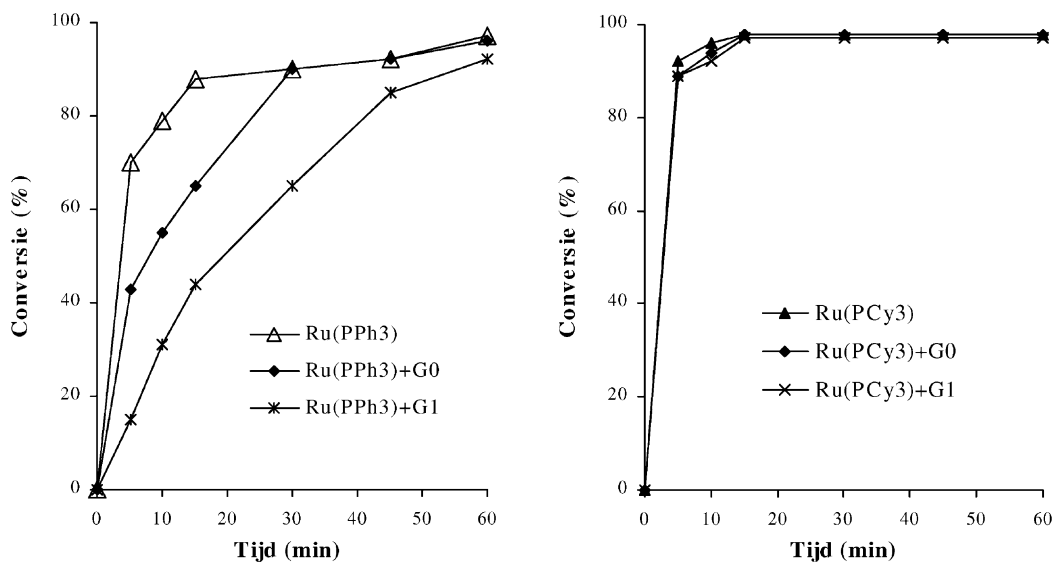
Fig. 2. Conversions of ROMP in function of time for the different Ru-systems. Reaction conditions: CH_2Cl_2, 25 °C, catalyst/monomer = 1/100 (per Ru-complex), [Ru-sites] = 2.5×10^{-3} M.

observed for the mononuclear Ru-catalyst compared to the polynuclear dendritic systems (Table 3).

With the polymerization conditions used in this study very narrow polydispersity values can be obtained with the PPh_3-based systems (Table 3). For the dendritic PCy_3-complexes (**5** and **6**) higher dispersities were obtained, in the same order of magnitude as for the mononuclear analogue [8].

The molecular masses of the polymers obtained with the different Ru-catalysts are summarized in Table 3. The mononuclear Ru-catalysts give rise to linear polymers, consequently the molar masses determined via GPC are in good accordance with the theoretical expected values. The same is observed for the catalysts based on G0 (**2** and **5**), which produce starpolymers with four branches. In these starpolymers there is only one branching point, as a result there is no remarkable difference in hydrodynamic volume compared to that of a free random linear polymer with the same molar mass. Hence, the actual

Table 3

Characterization of the polynorbornene(star)polymers synthesized with the different Ru-catalysts (**1–6**)

Catalyst	M_w[a]	M_n[a]	M_n[b]	PDI[a]	cis/trans[c]
$Ru(PPh_3)_2Cl_2(=CHPh)$ (**1**)	9700	8800	9238	1.10	13/87
$Ru(PPh_3)_2Cl_2(=CHPh)$ + G0 (**2**)	44400	37900	36349	1.17	12/88
$Ru(PPh_3)_2Cl_2(=CHPh)$ + G1Me (**3**)	53900	46100	69997	1.17	11/89
$Ru(Pcy_3)_2Cl_2(=CHPh)$ (**4**)	21000	10500	9332	2.0	16/84
$Ru(Pcy_3)_2Cl_2(=CHPh)$ + G0 (**5**)	63300	30500	37103	2.08	15/85
$Ru(Pcy_3)_2Cl_2(=CHPh)$ + G1Me (**6**)	90300	42700	73764	2.11	18/82

Reaction conditions: CH_2Cl_2, 25 °C, catalyst/monomer = 1/100 (per Ru-complex), [Ru-sites] = 2.5×10^{-3} M.

[a] Determined by GPC analysis, using a 60 cm, 1000 Å column from Tokyo Soda Manufacturing Co., refractive index (RI) detection (Melz) and $CHCl_3$ as eluent after calibration with polystyrene standards.

[b] Calculated by using the ratio catalyst/monomer and the conversion. In the calculation the mass of the dendritic core is included (G0 = 136 g/mol; G1Me = 584 g/mol).

[c] cis/trans ratio of the polynorbornene synthesized with the different Ru-catalysts, calculated from the ^{1}H-NMR spectra.
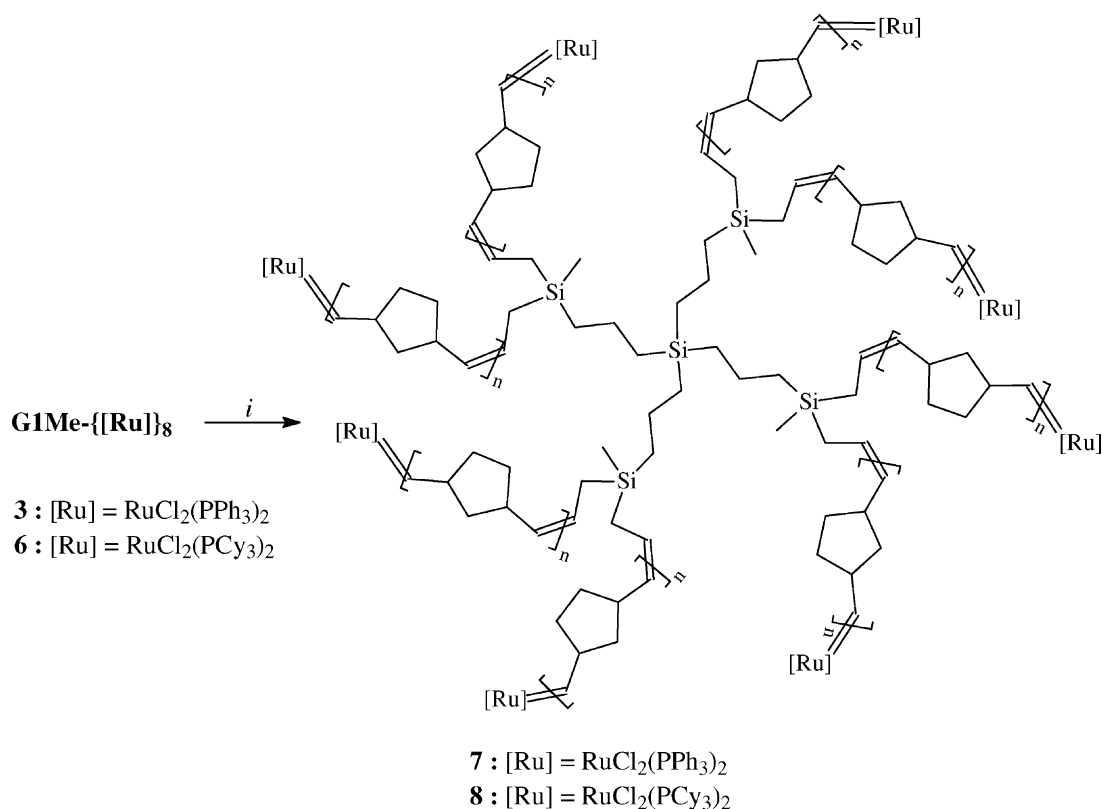
Scheme 1. Synthesis of starpolymers based on the first generation CS dendrimers with Ru–CS dendrimer catalysts; n: amount of monomerunits per arm, conversion-dependant. Reaction conditions: (i) 800 eq. or 200 eq. nbe, CH_2Cl_2, RT.

molecular masses determined by GPC are a good indication for the real values. However, for the first generation dendritic catalysts, conventional GPC analysis gives molar masses which deviate strongly from the calculated values. The presence of five branching points in the dendritic structure (Scheme 1) restricts its conformational freedom and lowers its hydrodynamic volume, resulting in lower observed values of molecular masses measured by GPC analysis. This

is clearly evidenced in Fig. 3 by the difference in theoretical M_n and the experimental M_n. Analogous deviations were observed when starpolymers with a CS core were synthesized via anionic or radical polymerization [9–11].

Since, the GPC analyses give systematically too low values for the first generation starpolymers, an additional analysis technique has been used for the determination of the molar mass. The molar mass of

Table 4
Comparison of the molar mass of the starpolymer (**7**) determined via ^{1}H-NMR and GPC

Catalyst	M_n (^{1}H-NMR)	M_n (GPC)	M_n[a]	PDI
Ru(PPh$_3$)$_2$Cl$_2$(=CHPh) + G1Me (**3**)	17300[b]	11600	18021	1.16

Reaction conditions: CH_2Cl_2, 25 °C, 60 min, catalyst/monomer = 1/25 (per Ru-complex), [Ru-sites] = 2.5×10^{-3} M.

[a] Calculated on the basis of the catalyst/monomer ratio, taking the conversion and the mass of the core into account.
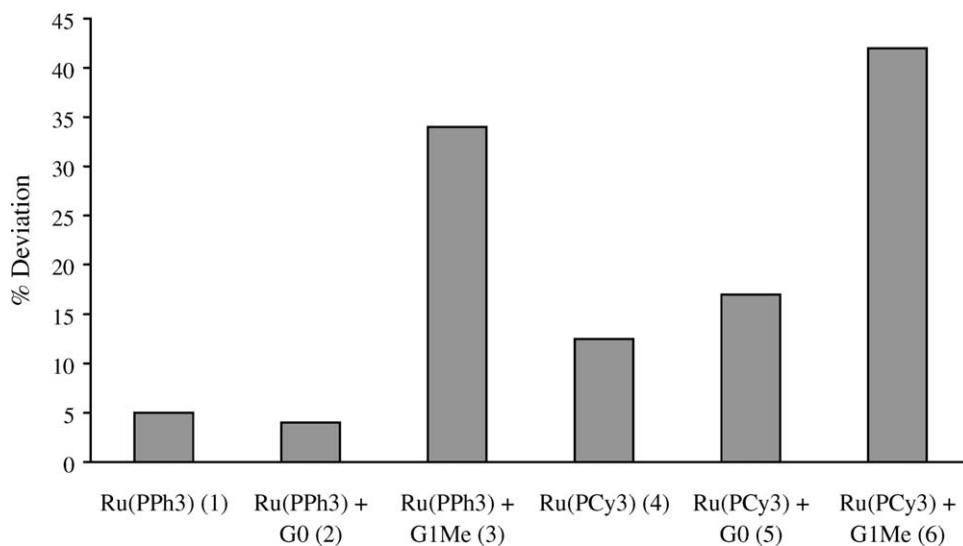[b] Taking the conversion and the mass of the dendritic core into account.

Fig. 3. Absolute value of the deviation (in terms of percentage) between the experimental M_n (GPC) and the calculated M_n for the polynorbornene synthesized with the different Ru-catalysts (**1–6**).

starpolymer **7** has been evaluated via the ^{1}H-NMR-spectrum, by comparison of the integration data of the protons of the double bonds in the polymer chain to the integration data of the CH_2-protons of the CS core (Table 4). For a more accurate analysis the polymerization is performed with a lower catalyst/monomer ratio (1/25). The mass obtained via ^{1}H-NMR approximates very well the mass based on the catalyst/monomer ratio. The mass obtained via GPC is dramatically lower compared to the mass obtained by means of ^{1}H-NMR. These results strongly support the proposed star-shaped structure of the obtained polynorbornene. The higher polydispersities in the PCy_3-based starpolymer prevent an accurate analysis of the molar mass via ^{1}H-NMR.

4. Conclusion

In conclusion, in this report dendritic multi-nuclear Ru-catalysts for the ring-opening polymerization of norbornene are evaluated. With this new dendritic core molecules starpolymers with four and eight branches can be synthesized in a controlled way. Only the shape of the polymer is influenced by these new catalysts, the activity and the selectivity are similar when compared to the mononuclear analogues.

The study of molar masses shows clearly that this concept of multi-dendritic ROMP catalysts can be successfully used for the synthesis of well-defined star-shaped polymers with a predictable molecular weight.

Acknowledgements

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