

# Low-generation carbosilane dendrimers as core for starpolymers using a Ru–ROMP catalyst

Herlinde Beerens, Francis Verpoort, Ludo Verdonck \*

*Department of Inorganic and Physical Chemistry, Organometallics and Catalysis Division, Ghent University, Krijgslaan 281, B-9000 Ghent, Belgium*

Received 13 June 1999; accepted 13 September 1999

## Abstract

Synthesis of new metathesis initiators by coupling Ru-complexes to low generation carbosilane dendrimers (G0–Ru, G1–Ru). These initiators show a very high activity for the ROMP of NBE. Using these dendrimer complexes, multi-arm starpolymers can be developed in a controlled manner. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Ru–carbene; Carbosilane dendrimers; Starpolymers; Ring-opening metathesis polymerization

Olefin metathesis has emerged as a powerful synthetic tool for the formation of C=C double bonds [1].

The most active metathesis catalysts are based on W and Mo [2–6], but these early transition metal complexes are very sensitive to functionalities. However, Grubbs et al. [7–10] synthesized homogeneous Ru–alkylidene complexes which are not only highly active for ROMP, but also possess a remarkable stability towards functional groups and protic media.

In 1995, Nguyen and Grubbs [11] synthesized heterogeneous Ru-catalysts via attaching  $\text{Cl}_2(\text{PR}_3)_2\text{Ru}=\text{CH}-\text{CH}=\text{CPh}_2$  on a 2% cross-linked polystyrene–divinylbenzene solid

support. These catalysts are active but the metathesis reaction is retarded.

Moreover, these PS–DVB-supported Ru–carbenes are not selective because of the different number of links formed at different reaction sites. The Ru-complexes are anchored to the support by a phosphine exchange reaction which is an equilibrium. Using this route, mixed-phosphine species are formed which decrease the reaction rate.

The polydispersity indices (PDIs) for the polymerization of NBE, with these supported catalysts, are high, due to the slow initial rate (Table 1).

In this respect, dendrimers can offer a solution. The regular occupation of the surface and the good accessibility of all the active catalytic sites for the reactants favour a high activity and selectivity. Besides, product separation is possible via (ultra)filtration [12,13].

\* Corresponding author. Tel.: +32-9-264-44-42; fax: +32-9-264-49-83.

*E-mail address:* ludo.verdonck@rug.ac.be (L. Verdonck).

Table 1  
Comparison of the PDI of polynorbornene synthesized with different Ru-initiators<sup>a</sup>

Initiator	PDI <sup>b</sup>	In/monomer <sup>c</sup>	Reference
Ru(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (=CHPh)	1.04	1/100	[7]
Ru(PCy <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (=CHPh)	2–2.5	1/100	[7]
Ru(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (=CH–CH=CPh <sub>2</sub> )	1.25	1/100	[7]
Ru(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (=CHPh) + G0	1.61	1/482	This work
Ru(PCy <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (=CHPh) + G0	2.47	1/500	This work
Ru(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (=CHPh) + G1	1.79	1/100	This work
Ru(PCy <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (=CHPh) + G1	3.2	1/100	This work
PS-DVB + Ru(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (=CH–CH=CPh <sub>2</sub> ) <sup>d</sup>	5.5	1/150	[11]

<sup>a</sup> Conditions: in CH<sub>2</sub>Cl<sub>2</sub>; 25°C.

<sup>b</sup> Determined by GPC-analysis, using a 60 cm 1000 Å column from Tokyo Soda Manufacturing, refractive index (RI) detection (Melz) and CHCl<sub>3</sub> as eluent after calibration with polystyrene standards.

<sup>c</sup> Ratio of the Ru-initiator to norbornene for ROMP.

<sup>d</sup> Conditions: in C<sub>6</sub>H<sub>6</sub>; 25°C.

Thus, by coupling Ru-alkylidene complexes to the boundary of carbosilane dendrimers, the advantages of homogeneous and heterogeneous catalysts [14,15] can be combined.

Using an excess of substrate, Uskakov et al. [16] observed ring closing metathesis (RCM) with tetraallylsilane (G0).

In this work, the catalyst/dendrimer ratio is 4:1 for the zeroth generation and 8:1 for the first generation. In this way, RCM is suppressed since all the double bonds of the dendrimers are immediately converted into Ru-carbenes.

In this communication, we present preliminary results in this field.

For the preparation of the Ru-carbenes, we use the route developed by Grubbs and et al. [7–10]. The zeroth generation of the carbosilane dendrimer (G0) is synthesized by the alkylation of SiCl<sub>4</sub> with allylmagnesiumbromide [17,18]. The first generation of the carbosilane den-

dimer is obtained by successive silylation (with dichloromethylsilane) and the alkylation (with allylmagnesiumbromide) of the zeroth generation.<sup>1</sup>

The attachment of the Ru-complexes to the boundary of the dendrimers is performed by an olefin metathesis reaction (Scheme 1). The Ru-complexes are dissolved in CH<sub>2</sub>Cl<sub>2</sub> and the dendrimers are added in a 4:1 ratio for the zeroth generation and in a 8:1 ratio for the first generation. The solution is stirred for ±20 h (for the PCy<sub>3</sub>-initiator, ±36 h for the PPh<sub>3</sub>-initiator) at room temperature, under a continuous argon flow. After 1 h, a colour change from purple to brown (for the PCy<sub>3</sub>-initiator, and from green to brown for the PPh<sub>3</sub>-initiator) is observed. After evaporating the solvent and washing with MeOH, an oily liquid remain in 85% yield. This compound is characterized by <sup>1</sup>H and <sup>13</sup>C NMR.

As shown in Table 2, there is a shift of the NMR-resonances of the alkylidene moiety to higher field after the reaction with the dendrimers. This can be attributed to the presence of the Si atom.

In the higher generations, the high-field shift increases. For the Ru-complex with the PCy<sub>3</sub>-ligands, an unresolved broad singlet was observed for the carbene proton.

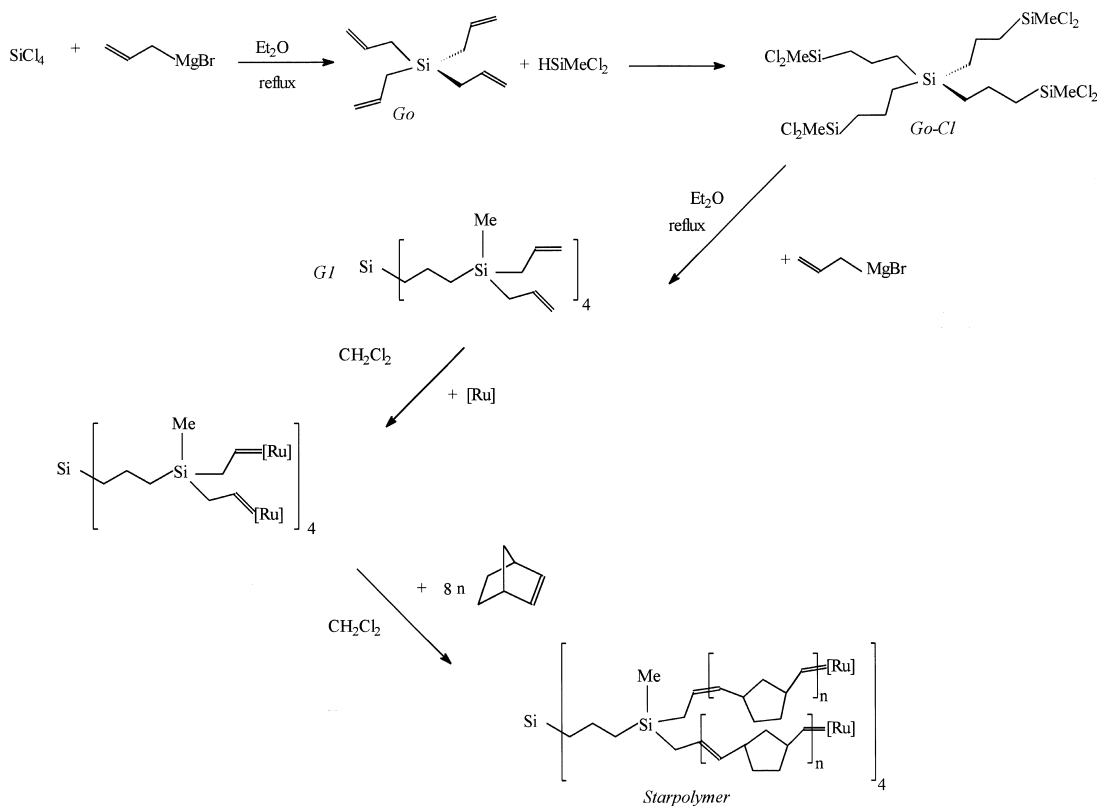
The catalytic activity of the dendrimer-initiator towards ROMP has been studied with norbornene as model substrate (Scheme 1).

The dendrimer-initiators were dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> and then the monomer was added. The reaction mixture was stirred at room temperature and the polymerization was terminated with MeOH [19].

The nature of the alkylidene moiety influences the structure of the synthesized polymers.

The PDIs and the *c/t* ratio of the synthesized polymers are influenced by anchoring the

<sup>1</sup> Synthesis of G1 is performed at the University of Amsterdam, Van't Hoff Research Institute, Inorganic Chemistry and Homogeneous Catalysis (P.W.N.M. van Leeuwen, J.C. de Wilde, J. Reek).



Scheme 1. Synthesis of the G1-dendrimer-initiator and starpolymer.

Ru-complexes to the dendrimer. If we compare the PDI of the polymers, synthesized by the different Ru-catalysts, we observe an increase

of the PDI by anchoring the Ru-carbenes on the dendrimers (Table 1). A possible explanation is a slower initiation rate. By using higher genera-

Table 2  
NMR-data of the Ru-initiators and *c/t* ratio of polynorbornene

Initiator	$[\text{Ru}] = \text{CHR}^a \text{ } ^{13}\text{C}$ (in $\text{CDCl}_3$ )	$[\text{Ru}] = \text{CHR}^a \text{ } ^1\text{H}$ (in $\text{CDCl}_3$ )	In/monomer <sup>b</sup>	<i>c/t</i> (in %) <sup>c</sup>
$\text{Ru}(\text{PPh}_3)_2\text{Cl}_2(\text{=CHPh})$	310	19.35 ( <i>t</i> , $J_{\text{P-H}} = 10.2$ Hz)	1/100	13/87
$\text{Ru}(\text{PPh}_3)_2\text{Cl}_2(\text{=CHPh}) + \text{G0}^d$	230	16.2–16.78 ( <i>m</i> )	1/482	12/88
$\text{Ru}(\text{PPh}_3)_2\text{Cl}_2(\text{=CHPh}) + \text{G1}$	184	16.34–16.2–15.99 ( <i>m</i> )	1/100	11/89
$\text{Ru}(\text{PCy}_3)_2\text{Cl}_2(\text{=CHPh})$	294	20.02 ( <i>s</i> )	1/100	16/84
$\text{Ru}(\text{PCy}_3)_2\text{Cl}_2(\text{=CHPh}) + \text{G0}$	230	18.9 ( <i>br.s</i> )	1/500	15/85
$\text{Ru}(\text{PCy}_3)_2\text{Cl}_2(\text{=CHPh}) + \text{G1}$	204	18.87 ( <i>br.s</i> )	1/100	18/82

<sup>a</sup>All the other NMR signals have been omitted for simplicity.

<sup>b</sup>Ratio of the Ru-initiator to norbornene for ROMP.

<sup>c</sup>*Cis/trans* ratio of polynorbornene synthesized with the different Ru-initiators, calculated from the  $^1\text{H}$  NMR spectra.

<sup>d</sup>A typical polymerization reaction proceeds as follows: 6.06 mg (2.075  $\mu\text{mol}$ ) of G0–Ru and 0.3769 g (4 mmol) norbornene were dissolved in  $\text{CH}_2\text{Cl}_2$  (7 ml) and the mixture is stirred at room temperature for 45 min. A brownish gel is formed and poured into vigorously stirred methanol to give a white precipitate and a brown solution.

tion dendrimers the increase of the PDI is even more pronounced. However, this increase is much lower compared to the PDI-enhancement as a consequence of the immobilisation of the vinylalkylidene-complex on the PS–DVB-support.

Furthermore, since there are no additional low mass peaks in the GPC-spectra, we can conclude that backbitting can be neglected.

By connecting the Ru-complexes to the dendrimer by the carbene function, we avoid the problem of the mixed-phosphine species. When the cyclic olefin is added, ROMP occurs in such a way that the monomer always slides in via the carbene bond (between dendrimer and ruthenium). In this way, the Ru-complexes remain at the periphery. These results demonstrate a facile synthetic route for the synthesis of starpolymers (Scheme 1). Variation in the architecture of the dendritic core can produce starpolymers with different branches [18]. Also, other kinds of dendrimers can be used. The only condition is that the linkage of the Ru-complexes to the dendrimer has to be made via the carbene function. Thus, commercial dendrimers such as polypropyleneimine [20] can be used. In combination with variation in the kind of monomer a multiplicity of possibilities for the synthesis of starpolymers is obtained.

Starpolymers are very interesting for microemulsions, emulsifiers, compatibilizers. Solutions and melts are expected to have an interesting potential in certain coating applications [21].

With this new concept, existing polymers can be made in a total new shape: the polymer arms are connected to one point in space.

In conclusion, we have developed a new class of metathesis initiators by using low generation dendrimers as ligand. This is an interesting extension of the applications of dendrimers: (1) immobilisation of Grubbs-catalysts to the dendrimeric boundary and (2) dendrimers as core for multi-arm starpolymers.

Work is in progress to use higher generations of the dendrimers, and to do further catalytic experiments with this new Ru-initiators.

## Acknowledgements

This work was supported by het wetenschappelijk onderzoeksfonds — Flanders (Belgium) (F.W.O.). H.B. is indebted to I.W.T. for positon as research assistant. We also thank the Laboratory of Inorganic Chemistry and Homogeneous Catalysis of the University of Amsterdam for their contribution in the synthesis of the G1-dendrimer.

## References

- [1] K.J. Ivin, J.C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, London, 1997.
- [2] K.J. Ivin, *Olefin Metathesis*, Academic Press, London, 1983.
- [3] R.R. Schrock, J.S. Murdzek, G.C. Bazan, J. Robbins, M. Dimare, M. O'Regan, *J. Am. Chem. Soc.* 112 (1990) 3875.
- [4] P. Dounes, W.J. Feast, A.M. Kenwright, *Polymer* 36 (14) (1995) 2878.
- [5] V. Heroguez, M. Fontanille, *J. Polym. Sci., Part A: Polym. Chem.* 32 (1994) 1755.
- [6] D.L. Barnes, N.W. Eilerts, J.A. Heppert, W.H. Huang, M.D. Morton, *Polyhedron* 13 (18) (1994) 1267.
- [7] P. Schwab, R.H. Grubbs, J.W. Ziller, *J. Am. Chem. Soc.* 118 (1996) 100.
- [8] E.L. Dias, S.T. Nguyen, R.H. Grubbs, *J. Am. Chem. Soc.* 119 (1997) 3887.
- [9] S.T. Nguyen, R.H. Grubbs, *J. Am. Chem. Soc.* 115 (1993) 9858.
- [10] Z. Nu, S.T. Nguyen, R.H. Grubbs, J.W. Ziller, *J. Am. Chem. Soc.* 117 (1995) 5503.
- [11] S.T. Nguyen, R.H. Grubbs, *J. Organomet. Chem.* 497 (1995) 195.
- [12] J.W.J. Knapen, A.W. van der Made, J.C. De Wilde, P.W.N.M. van Leeuwen, P. Wijkens, D.M. Grove, G. van Koten, *Nature* 372 (1994) 659.
- [13] J. Alper, *Science* 251 (1991) 1562.
- [14] D.A. Tomalia, P.R. Dvornic, *Nature* 372 (1994) 617.
- [15] R.F. Service, *Science* 267 (1995) 458.
- [16] N.V. Uskakov, E.B. Portnykh, N.A. Pritula, E.S. Finkel'shtein, *Izv. Akad. Nauk SSSR, Ser. Khim.* 38 (1989) 2797.
- [17] A.W. van der Made, P.W.N.M. van Leeuwen, *J. Chem. Soc., Chem. Commun.* (1992) 1400.
- [18] A.W. van der Made, P.W.N.M. van Leeuwen, J.C. de Wilde, R.A.C. Brandes, *Advanced Materials* 5 (1993) 466.
- [19] I. Del Río, G.v. Koten, *Tetrahedron Lett.* 40 (1999) 1401.
- [20] E.M.M. De Brabander-Van den berg, A. Nijenhuis, M. Mure, J. Keulen, R. Reintjens, F. Vandenbooren, B. Bosman, R. DeRaaf, T. Frijns, Wal Svd *et al.*, *Macromol. Symp.* 77 (1994) 51.
- [21] T.B. Kimmel, ICPET, Ottawa, Ontario, K1A0R6, Canada, <http://www.icpet.nrc.ca/tops/top5-e.html>.