A new ROMP W-initiator as model for W-carbosilane dendrimers for the synthesis of starpolymers

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Abstract

A new Ring Opening Metathesis Polymerization (ROMP)-initiator based on an aryloxy–tungsten complex (activated with Me_4Sn) anchored on the lowest generation of a carbosilane dendrimer (G0) has been synthesized. The catalytic activity of the W-initiator is studied for the ROMP of norbornene as model substrate, generating starpolymers. However, after complete conversion of the monomer, the Si-core starpolymers react further by a dismutation reaction resulting in branched high molecular weight starpolymers. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Olefin metathesis is very interesting in the areas of polymer chemistry and synthetic organic chemistry. The design of versatile, highly active and well-characterisized catalysts remains one of the main objectives of the research in olefin metathesis [1,2].

Tungsten(VI)aryloxide complexes of the type $W(OAr)_nCl_{6-n}$ (OAr = unsubstituted or substituted phenoxides) are easily synthesized from WCl_6 and phenol derivates [3,4]. These com-

plexes are known to provide very active metathesis catalysts in the presence of a cocatalyst like $EtAlCl_2$, $Et_3Al_2Cl_3$ or R_4M (R = methyl or butyl, M = Sn or Pb) [5–9]. Furthermore, they give rise to a high stereoselectivity in the metathesis of internal and terminal olefins and olefinic esters [5,8–10].

The electronic and steric properties of the various aryloxide ligands can be varied by changing the number, the nature and the position of the substituent(s) on the aryloxide [5–9]. Increasing the electron-withdrawing properties of the aryloxide ligands results in an increase of the metathesis activity. Complexes with electron-withdrawing substituents on positions 2 and 6 of the aryloxide ligand were found to be superior for metathesis of alkenes, compared to the other aryloxide ligands. Besides the elec-

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tronic and steric properties, the phenoxide groups of these W-catalysts also increase the solubility and stability of the complexes [11].

Many different homogeneous catalytic systems were developed, but they show difficulties with respect to separation and recuperation.

In 1997, our group synthesized heterogeneous W-catalysts by immobilization of tungsten–phenoxide complexes [W(O-2, 6-C_6H_3-$X_2)_2Cl_4$ (X = t-Bu, Me, Br, Cl)] on a silica [11] and a silica–niobia support [12]. An advantage of these heterogeneous systems is the easy recuperation possibility. However, these catalysts show a lower selectivity compared to homogeneous homologues in the metathesis reaction of 2-pentene due to the diversity of the active sites.

In this context, dendrimers can offer a solution. By linking the metalalkylidene complexes to the dendrimer surface, the link between homogeneous and heterogenous catalysis can be made : product separation becomes possible via (ultra)filtration and the good accessibility and specificity of all the active sites is responsible for a high activity and selectivity.

Furthermore, when the complexes are linked to the dendrimer surface via the alkylidene function, the dendrimer can be used as core for starpolymers.

2. Discussion

The work presented here includes preliminary results in the field of this last topic. W(O-2, 6-$C_6H_3Cl_2)_2Cl_4$ is activated with Me_4Sn and anchored on a surface of a carbosilane dendrimer model compound (tetraallylsilane). This W-system has been investigated as catalytic system for the Ring Opening Metathesis Polymerization (ROMP) of norbornene and is an extension on earlier work in this field, describing the synthesis of Ru-carbenes combined with low generation carbosilane dendrimers [13].

For the synthesis of the 2,6-disubstituted aryloxidecomplexes of W(VI), we have used the

method of Funk and Baumann [3] and Quignard et al. [4]:

$$WCl_6 + 2HO\text{-}2,6\text{-}C_6H_3Cl_2$$

$$\xrightarrow[\text{reflux}]{CCl_4} W(O\text{-}2,6\text{-}C_6H_3Cl_2)Cl_4 + 2HCl. \qquad (1)$$
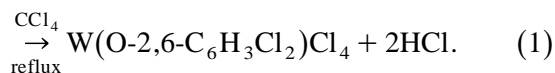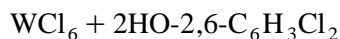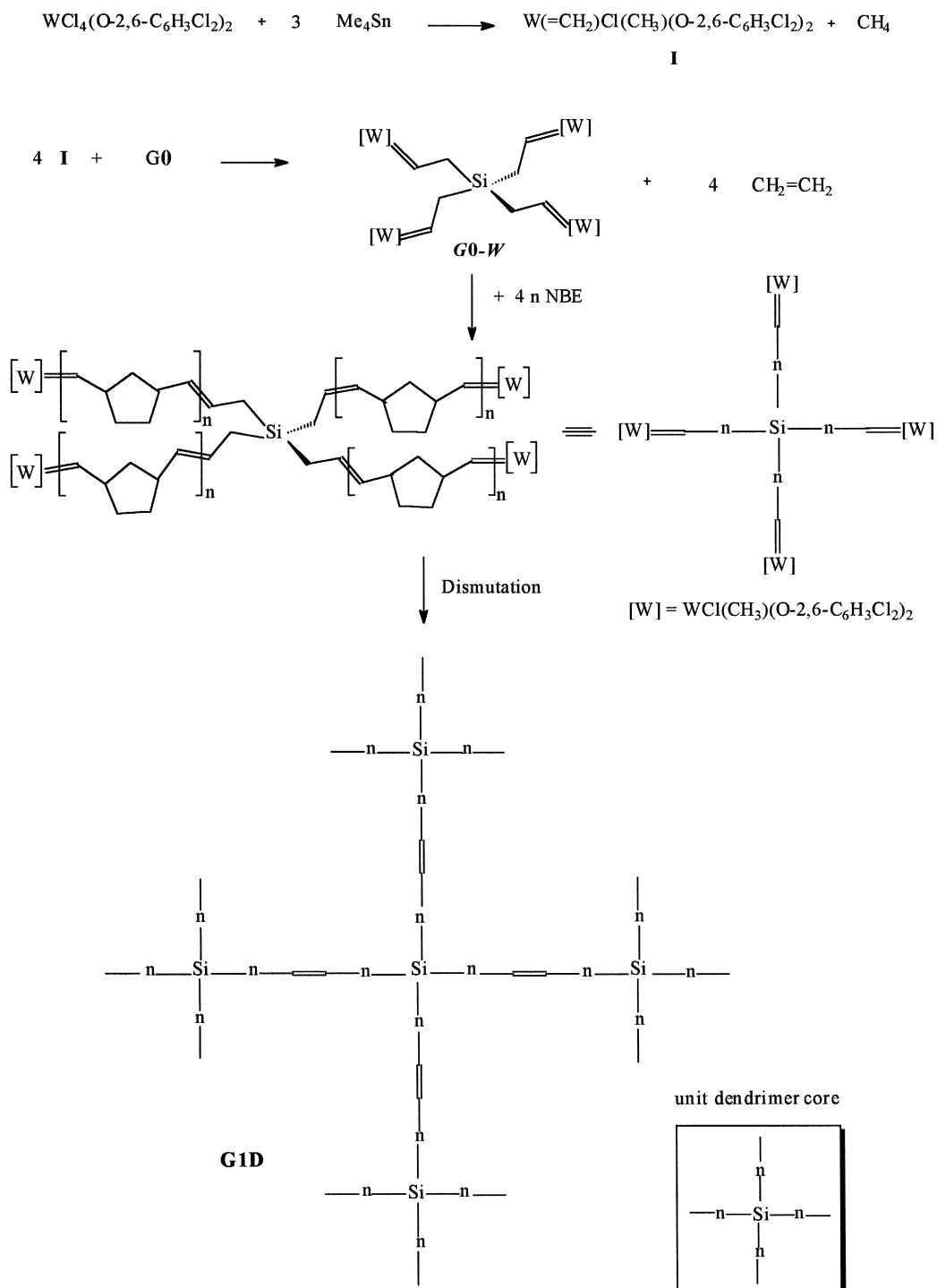
Black microcrystals of this tungsten-precursor were obtained in a yield of 80%.

For the activation, the tungsten precursor (1 equiv.) was dissolved in chlorobenzene, followed by the addition of the cocatalyst, Me_4Sn (3 equiv.), changing the colour from brown to red. The catalyst system was heated at 65°C and after 20 min of activation 0.25 equiv. of the zeroth generation of the carbosilane dendrimer, synthesized according to van der Made et al. [14,15] was added. The solution was stirred for another 90 min at 65°C under an inert atmosphere followed by evaporation of the solvent resulting in a dark-brown oily liquid.

The reaction has been screened by gas chromatography. In the activation step, the formation of methane and a small amount of ethene has been detected. Methane is formed by the double alkylation of W, followed by α-H elimination [8]. Ethene formation (0.02 equiv.) is indicative for deactivation of W by coupling between two tungsten–alkylidene species. This is in good agreement with the results of Basset [8]. It must be noted that the amount of deactivated species was taken into account when the tungsten complexes were coupled with the dendrimer. On addition of the tetraallylsilane, the evolution of ethene increased (0.99 equiv.), due to the metathesis reaction between the carbosilane dendrimer and the W-methylene species (Scheme 1).

The coupling reaction has been followed with Raman spectroscopy : the disappearance of the allylic double bond at 1631 cm^{-1} and the formation of the new signals at 3080 and 2945 cm^{-1} for the W-alkylidene bound were a clear indication for the link between the dendrimer and the W-complexes [16].

$$WCl_4(O\text{-}2,6\text{-}C_6H_3Cl_2)_2 \quad + \quad 3 \quad Me_4Sn \quad \longrightarrow \quad W(=CH_2)Cl(CH_3)(O\text{-}2,6\text{-}C_6H_3Cl_2)_2 \quad + \quad CH_4$$
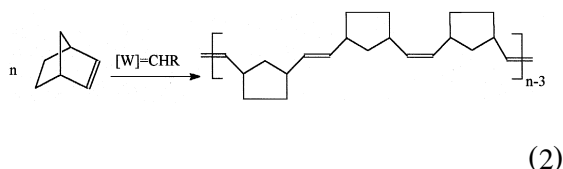
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Scheme 1. Synthesis of starpolymers by dismutation.

The W-aryloxide complexes/Me_4Sn anchored on the carbosilane dendrimer pheriphery

were used for the polymerization of norbornene via ring opening metathesis in dry chloroben-

zene (Eq. (2); a typical polymerization procedure is given in footnote f of Table 1).

$$(2)$$

The reaction mixture was stirred at room temperature and the polymerization was terminated with MeOH at different run times. Structural characterization of the polymers was accomplished by ^{1}H NMR. Remarkable is the high degree of *trans*-linkages (Table 1). Contradictory to previously reported tungsten systems, showing a high *cis* C=C bond content in the polymers [17,18]. In general, only Ru-systems are known to generate polymers, having a high *trans* C=C bond content [19].

The polydispersities obtained by GPC analysis of the norbornene polymers are relatively low compared to the Grubbs-initiator anchored on the zeroth generation of the carbosilane dendrimers (Table 1) [13].

Analysis of the molecular weights indicate that W-alkylidenes present on the carbosilane

pheriphery react mutually by an intermolecular metathesis reaction. In each dimerization reaction, two metal complexes are deactivated due to a dismutation, resulting in a coupling between two dendrimer units (Scheme 1). As a result, two metal complexes (one of each dendrimer branch) are eliminated from the dendrimer surfaces and an unidentified tungsten species is formed.

By increasing the reaction time, more W-carbenes undergo this dismutation, resulting in high MW branched starpolymers. However, this growth is finite: after about 20 min of polymerization, the size of the starpolymers remains nearly constant (Table 1).

An explanation for this "phenomenon" may be the high activity of the W-alkylidene dendrimer system. This is in contrast with the corresponding Ru-alkylidene dendrimer catalysts, where no dismutation was observed [13].

As it is expected for a star-shaped polymer, the molecular weight determined from the elution volume by comparison with narrow molecular weight polystyrene standards results to be considerably lower than the calculated molecular weight (Table 1) [20].

Table 1
GPC-data and NMR-data of the starpolymers

Reaction time	I/M[a]	M_w[b]	M_n[b]	M_n[c] (calc.)	PDI[b]	c/t[d]	Size[e]
5′	1/100	523,700	279,500	526,800	1.87	23/77	G1D + 9
20′	1/115	989,200	638,200	995,200	1.55	23/77	G2D + 6
45′	1/97	834,500	678,400	839,500	1.23	21/79	G2D + 6
60′	1/103[f]	885,900	503,300	891,200	1.76	23/77	G2D + 6

[a] For all the experiments is the monomer conversion roughly 100%. Ratio of the W-initiator to the monomer for ROMP (expressed in monomer units/W-complex).

[b] Determined by GPC-analysis, using a 60-cm 1000-Å column from Tokyo Soda Manufacturing, refractive index (*RI*) detection (Melz) and CHCl$_3$ as eluent after calibration with polystyrene standards.

[c] Calculated from the monomer to initiator ratio. M_n(calc.) = $M/I \times 4 \times$ MM (nbe) + MM (Si + 4 $\times$ CH$_2$CH).

[d] *Cis/trans* ratio of polynorbornene synthesized with the W-initiator, calculated from the ^{1}H NMR spectra.

[e] The size of the branched starpolymers is determined by division of the molecular weight, obtained via GPC, by the molecular weight of one unit dendrimer core. The size is expressed in generation of the dendrimer (G1D = 5 unit dendrimer cores, G2D = 17 unit dendrimer cores) + the additional amount of unit dendrimer cores. A unit dendrimer core is specified in Scheme 1. G1D = G0−W of which each of the 4 W-complexes undergo dismutation. G2D = G1D of which each of the 12 W-complexes undergo dismutation.

[f] A typical polymerization reaction proceeds as follows: 0, 18 g (0,076 mmole) of G0 − W and 2, 9 g (31 mmole) norbornene are dissolved in PhCl (7ml) and the mixture is stirred at room temperature for 60 min. A brownish gel is formed and poured into vigorously stirred methanol to give a white precipitate and a brown solution.

3. Conclusion

In this paper, a model method for the synthesis of W-initiators based on carbosilane dendrimers is described. This W-system shows a high activity towards the ROMP of NBE. This findings also demonstrate a convenient route to the synthesis of star shaped polymers via ring opening metathesis polymerization.

In future work, we will explore the combination of the W-initiators to higher generations of carbosilane dendrimers.

Acknowledgements

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