 DOI: 10.1002/masy.200900046

Ring-Opening Metathesis Polymerization of Cyclooctyne Employing Well-Defined Tungsten Alkylidyne Complexes

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Summary: The ring-opening metathesis polymerization of cyclooctyne was studied was studied in the presence of catalytic amounts of the tungsten alkylidyne complexes $[RC{\equiv}W(NIm^{tBu})\{OCMe(CF_3)_2\}_2]$ (**1a:** R = CMe_3, **1b:** R = Ph). The resulting polymers show relatively narrow polydispersities with the PDI ranging from 1.2 to 2.4. Treatment of **1b** with cyclooctyne in dilute toluene or hexane solution afforded only low molecular weight oligomers. The mass spectra of these oligomers indicate the existence of macrocycles of the formula $[C(CH_2)_6C]_n$ (n = 3–9). In contrast, reactions at high substrate concentration led to mixtures of cyclic oligomers and linear polymers, which is probably a result of ring-chain equilibria, established in agreement with the Jacobson-Stockmayer theory of macrocyclization. In contrast, treatment of neat cyclooctyne with a catalytic amount of the catalyst produced medium molecular weight polymers in good yields.

Keywords: catalysis; cyclopolymerization; polyacetylenes; polycyclooctyne; ring-opening metathesis polymerization (ROMP); tungsten alkylidyne complexes

Introduction

The ring-opening metathesis polymerization (ROMP) of cyclic olefins has become an important synthetic tool in polymer chemistry.[1] The great success of this method is based on the availability of a large number of well-characterized transition metal alkylidene complexes that have been established as highly efficient catalyst systems during the past decades.[2] In contrast, the related ring-opening metathesis of cyclic alkynes has been only scarcely studied,[3,4] despite the availability of a number of well-defined alkyne metathesis catalysts.[5] The first example of ring-opening alkyne polymerization was reported by Schrock and coworkers in the late 1980s, who demonstrated that the polymerization of the strained monomer cyclooctyne is efficiently catalyzed by molybdenum and tungsten alkylidyne complexes of the type $[M(CR)(OR')_3]$ (M = Mo, W; R = Pr, *t*Bu; R' = *t*Bu, 2,6-diisopropylphenyl) (Scheme 1). This study showed that both polymers and cyclic oligomers are formed in agreement with the Jacobson-Stockmayer theory of macrocyclization.[6]

Lately, we have introduced a new design strategy for the development of highly efficient alkyne metathesis catalysts that involves the combination of electron-withdrawing alkoxides with strongly electron-donating imidazolin-2-iminato ligands.[7] The most active species of this type, the neopentylidyne complex **1a**, exhibits high catalytic activity even at room temperature and allows for efficient alkyne cross metathesis (ACM) of phenylpropynes and ring-closing alkyne metathesis (RCAM) of α,ω-diynes.[7–9] This activity suggested that **1a** should also promote ring-opening alkyne polymerization, and the present study describes the ROMP of cyclooctyne in the presence of catalytic amounts of **1a** and

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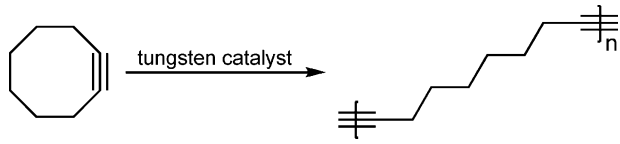


Scheme 1.
ROMP of cyclooctyne.

of its benzylidyne congener **1b** (Scheme 2). Whereas **1a** has been prepared via a *high oxidation route* from WCl_6, the latter complex has become available only recently following a *low oxidation state route* starting from $W(CO)_6$.[10]

Results and Discussion

Preparation

In a typical procedure, a toluene or *n*-hexane solution of cyclooctyne[11] was added to a solution of the catalyst in the same solvent. The reaction mixture was stirred for 16 hours at room temperature, while white or pale yellow solids precipitated. Methanol was then added to the reaction mixture, and the insoluble part of the products was isolated by decantation and centrifugation and dried under high vacuum. The soluble part was also isolated by evaporation of the solvents. Some reactions were also performed in neat cyclooctyne. In these cases, red solids were formed within 15 minutes. The work-ups were carried out as described above.

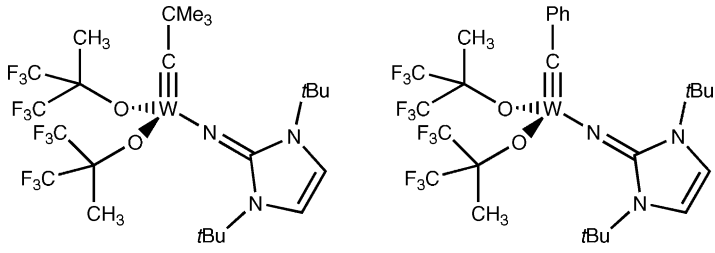
Characterization

The insoluble product fractions were characterized by gel permeation chromatography (GPC). For a typical procedure, THF was added to the sample, which normally did not dissolve completely even after being treated with ultrasound for hours. The sample was then filtered and analyzed by GPC. The GPC results are shown in Table 1.

Discussion

Entries 1 and 2 summarize the results for the ROMP of neat cyclooctyne in the presence of catalytic amounts (1 mol%) of the alkylidyne complexes **1a** and **1b**. As expected, both complexes exhibit a similar catalytic performance, and in both cases, a polymeric fraction is isolated in 70% or 80% yield, respectively, after quenching with methanol. GPC analysis reveals that medium weight polycyclooctynes with $M_n = 33000$ g/mol (**1a**) and $M_n = 26400$ g/mol (**1b**) with relatively narrow polydispersities ($PDI = M_w/M_n = 1.4, 1.6$) are formed.

Entries 3 – 6 show the influence of the substrate concentration on the yield and properties of the resulting polymer. These reactions were performed either in neat



Scheme 2.
Structures of the catalysts.

Table 1.
GPC Analysis of Polycyclooctyne.

Entry	mol% catalyst	Solvent	Substrate concentration [mol/L]	M_n [g/mol]	M_w [g/mol]	PDI	Polymer yield [%]
1	1[a]	–	neat	33000	46800	1.4	70
2	1[b]	–	neat	26400	41300	1.6	80
3	5[b]	–	neat	9960	23200	2.3	95
4	5[b]	toluene	0.03	82000	100000	1.2	7
5[c]	5[b]	toluene	0.02	–	–	–	0
6[c]	5[b]	*n*-hexane	0.02	–	–	–	0

[a]1a as catalyst. [b]1b as catalyst. [c]only cyclic oligomers were obtained.

cyclooctyne (entry 3) or in toluene or hexane solution (entries 4 – 6) using a 5 mol% catalyst loading of **1b**. A high yield (95%) of polymer was obtained, if the reaction was performed without any solvent. As expected, the higher catalyst concentration in comparison with entries 1 and 2 affords a lower molecular weight ($M_n = 9960$) and a polydispersity index (PDI) of 2.3. In contrast, the polymer yield is much lower (only 7%), if the reaction is performed in toluene with a substrate concentration of 0.03 mol/L. In this case, the polymeric material exhibits a significantly higher molecular weight ($M_n = 82000$) together with a relatively narrow polydispersity (PDI = 1.2). Decreasing the substrate concentration to 0.02 mol/L did not afford an insoluble polymeric fraction at all, and only soluble oligomers were formed. The same result was obtained by using *n*-hexane instead of toluene (entry 6).

This interesting concentration-dependence of the polymer/cyclooligomer yield could be explained by theories of ring-chain equilibria in ROMP, which is described in detail in a recent review published by Monfette and Fogg.[12] During ROMP, linear polymers are produced by release of ring strain in the cyclic monomers. However, cyclic oligomers may also form by means of cyclodepolymerization through polymer backbiting. In this case, a ring-chain equilibrium is established, which leads to a mixture of linear polymers and cyclooligomers. The distribution of these two species can be predicted by the Jacobson-Stockmayer (JS) theory.[6] According to this theory, there is a critical monomer concentration [M] or cut-off point at equilibrium, below which a distribution of cyclic oligomers exists, and above which the total concentration

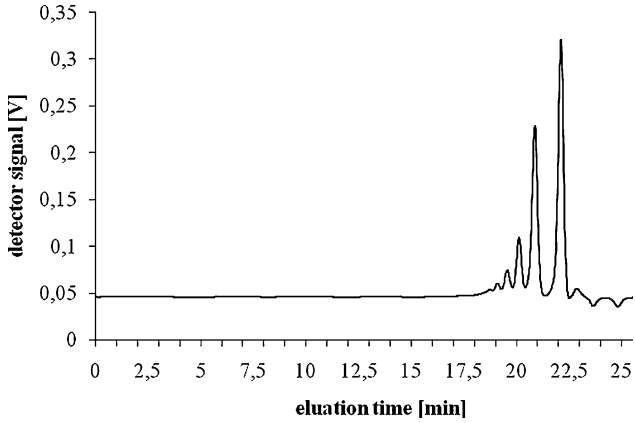


Figure 1.
GPC analysis of cyclic oligomers prepared by adding 20 eq of cyclooctyne to a solution of **1a** followed my quenching with methanol.

of the cyclic oligomers remains constant and linear polymers emerge. The JS theory also suggests that the formation of cyclic oligomers is favoured at lower concentration due to entropic effects, and our experimental data are in agreement with this theoretical prediction. Moreover, the formation of cyclooligomers was confirmed by GPC analysis and mass spectrometry. Figure 1 shows the GPC trace for the cyclic oligomers prepared by addition of 20 equivalents of cyclooctyne to a solution of **1b** in *n*-hexane, followed by quenching with methanol (entry 6). The different peaks in the GPC graph correspond to cyclic oligomers with a different number of monomer units. Mass spectra indicate that the mixture consists of cyclic oligomers with the formula $[C(CH_2)_6C]_n$ $(n = 3 - 9)$.

Conclusion

The present study shows that imidazolin-2-iminato tungsten alkylidyne complexes **1a** and **1b** are capable to efficiently catalyze the ring-opening metathesis polymerization of cyclooctyne. The polymer/cyclooligomer ratio depends on the substrate concentration, and lower substrate concentrations increase the yield of cyclooligomers, whereas predominant polymer formation is observed under neat reaction conditions. These results are in agreement with the Jacobson-Stockmayer theory of ring-chain equilibria. Further detailed studies are necessary to substantiate these findings and to fully uncover the behavior of highly active catalysts such as **1a** and **1b** in equilibrium ring-opening and also ring-closing alkyne metathesis.[8] These studies are particularly interesting in view of the large body of results available for equilibrium olefin metathesis.[12]

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