

New features of ROMP by heterogenization of molybdenum carbene complexes

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Abstract

An inorganic carrier based on alumina covered with methylaluminoxane (MAO) which had been crosslinked by various diols was used to immobilize molybdenum carbene complexes of the type $\text{Mo}(\text{CH-}i\text{-Bu})(\text{NAr})(\text{OC}(\text{CH}_3)_2\text{CF}_3)_2$ (**1**) and $\text{Mo}(\text{CH-}i\text{-Bu})(\text{NAr})(\text{OTf})_2(\text{dme})$ (**2**) ($\text{Ar}=2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2$). Employment of fluorinated diols heavily increased the activity in ring-opening metathesis polymerization (ROMP) of different substituted norbornenes, 2-azanorbornene, cyclooctene, cyclooctadiene and metathesis reaction of acyclic alkenes. Investigations were made on differences in stereochemistry of polymers obtained by these new supported complexes compared with homogeneous polymerization initiated by (**1**). The immobilized initiators produced polymers with a higher content of *trans* vinylene, particularly when monomers were substituted with bulky groups. Terminal alkenes like 1-hexene worked as chain transfer agents. Thus regulation of molecular weight was possible. In addition these supported carbene complexes showed a surprisingly high stability of the alkylidene species in suspension—even after 30 days of polymerization the activity was still about 15% of the initial value. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Metathesis; Molybdenum carbene complexes; Supporting; Heterogeneous catalysis

1. Introduction

Since the 1980s well-defined carbene complexes have been synthesized successfully [1,2]. These initiators provide a high activity in metathesis reactions and tolerate several functionalities of monomers [3]. Although ROMP is a living polymerization the active species usu-

ally cannot be separated for re-use afterwards. Generally the extraction of the metallic residue from the polymer is critical and often contamination of the polymer remains from the catalysts. Immobilization of these complexes, however, would solve these problems and provide an easier handling in technical employment. Immobilized catalysts are generally of growing interest, because they can combine the advantages of homogeneous and heterogeneous catal-

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ysis. Hereby, inorganic oxides like silica or alumina often serve as support materials. We tried to develop an inorganic carrier for the molybdenum carbene complexes of the type $\text{Mo}(\text{CH-}i\text{-Bu})(\text{NAr})(\text{OC}(\text{CH}_3)_2\text{CF}_3)_2$ (**1**) and $\text{Mo}(\text{CH-}i\text{-Bu})(\text{NAr})(\text{OTf})_2(\text{dme})$ (**2**) ($\text{Ar}=2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2$). This carrier is based on alumina which has been used as supporting material for metallocenes [4] for years now.

Few investigations have been made to support carbene complexes on different materials so far. Fischer carbene complexes were immobilized by a reaction with acidic OH-groups of silica yielding surface bonded carbenes [5,6]. Tris(neopentyl)nitridomolybdenum can be activated on silica under removal of neopentane [7]. Ruthenium carbene complexes of the type $\text{RuCl}_2(=\text{CHCH}=\text{CHPh})(\text{PR}_3)_2$ ($\text{R}=\text{Ph}, \text{Cy}$) were immobilized on a polymer matrix by ligand exchange [8] or by exchange of alkylidene moiety on a resin containing alkene groups [9]. In ROMP polymeric support materials often bear problems in diffusion due to swelling. Therefore polydispersity is usually rather high (PDI about 5.5 [8]). By the use of an inorganic carrier we hoped to diminish these problems.

In our investigations the chemical bonding of the initiator complex occurs via exchange of the alkoxy groups. So we are also able to immobilize and activate the inactive complex (**2**) simultaneously. This fact provides the reduction of the synthesis of the molybdenum complexes [1] by one step.

Similar to the homogeneous initiators the employment of fluorinated diols increases the activity of the supported catalysts so much that metathesis of acyclic olefins is possible, too. Terminal olefins can be used as chain transfer agents and therefore molecular weight can be regulated. On the other hand metathesis reaction of olefins provides the possibility to detach the polymer chains from the supported carbenes while the carbenes stay active. This makes recycling of catalysts possible and therefore shows interesting features for technological employment of these molybdenum complexes.

2. Experimental

All operations were carried out in an inert atmosphere with Schlenck techniques under Ar-

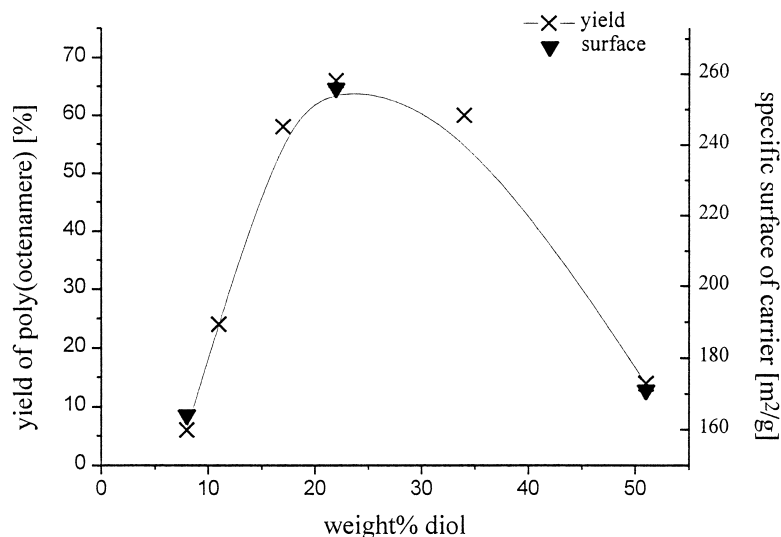
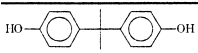
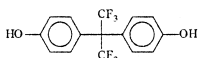


Fig. 1. Dependence of carrier's activity and surface on the wt.% of 4,4'-(hexafluoroisopropylidene)-diphenole.

Table 1
Dependence of activity on diols' electron-withdrawing substituents

Diol	Specific surface [m ² /g]	M _n	Polydispersity (M _w /M _n)	Yield [%] ^a
	256	2.0·10 ⁵	1.73	17%
	245	2.1·10 ⁵	1.68	67%

^a Polymerization of 300 mg cyclooctene with 30 mg heterogeneous initiator in 1 ml toluene.

gon or in a glove box under nitrogen. Solvents were dried with Na/K alloy, 1-hexene with CaH₂. Al₂O₃ was provided by Degussa (Al₂O₃ C).

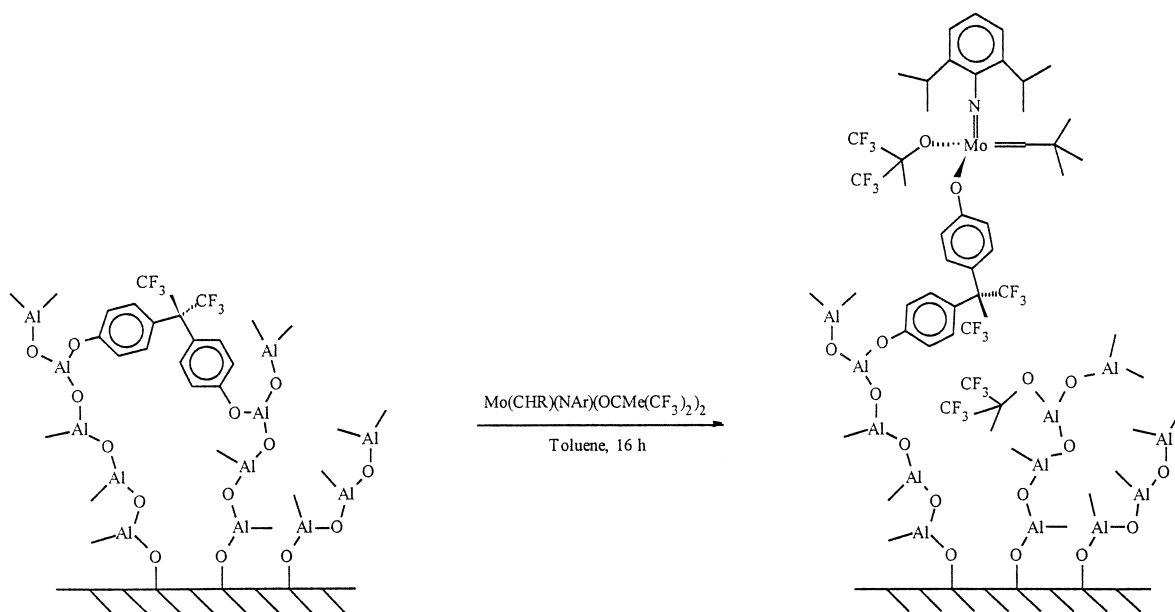
2.1. Preparation of carrier

The carrier is based on γ -alumina with a known amount of OH-groups on the surface. The alumina was suspended in toluene and treated with a solution of MAO (36 wt% in toluene; 1.8 ml g⁻¹ alumina) under stirring at

room temperature. Afterwards different diols solved in THF were added to crosslink MAO chains in order to increase the specific surface of the carrier and to immobilize and insolubilize the MAO [4]. The amount of diols was varied between 10 and 50 wt% (Fig. 1). Finally the white powder was dried in vacuum.

2.2. Supporting of complexes

The carrier (100 mg) was stirred in a solution of the molybdenum complex (1) or (2) (5.7



Scheme 1. Assumed mechanism of complex's (1) immobilization.

μmol) for 12 h at room temperature. We observed that higher temperature and longer time of supporting decreased the activity. Afterwards the heterogeneous catalysts were washed and centrifuged at least 5 times until the solutions did not polymerize norbornene any more. Therefore the influence of solved initiator during later polymerization could be neglected. The amount of molybdenum on the heterogeneous catalyst was found to be 0.51 wt% (5.3 μmol ; ICP-OES measurements).

2.3. Polymerization reaction

To a suspension of 30 mg heterogeneous catalyst (containing 1.6 μmol molybdenum

complex) in 1 ml toluene about 2.7 mmol of monomer was added. 14 h later the polymerizations were quenched by addition of benzaldehyde. After dilution with CH_2Cl_2 the heterogeneous catalysts were easily detached by centrifuging. The obtained polymer solutions were absolutely clear and transparent. The yield of polymer depended on the monomer and was usually between 75 and 100%. A rather small share of 50% was obtained with cyclooctadiene. Polydispersity of the polymers was about 1.5–1.8.

Investigations were made to re-use the initiator. Monomer and 1-hexene in different ratios were added to the heterogeneous initiator. After 3 days the initiator was removed by centrifuga-

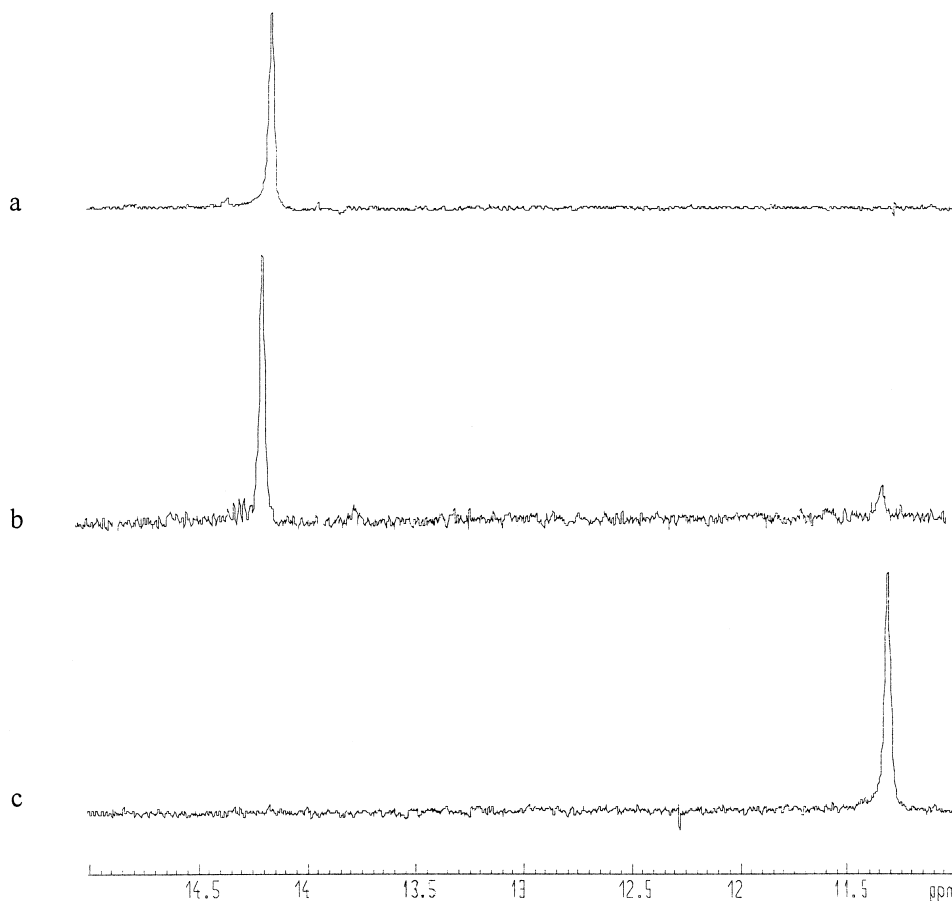


Fig. 2. 90 MHz ^1H NMR experiment of reaction of $\text{Al}(\text{O}-t\text{-Bu})_3$ with triflate complex (only carbene region): (a) triflate complex, (b) triflate complex and $\text{Al}(\text{O}-t\text{-Bu})_3$ after 10 min, (c) $\text{Mo}(\text{CH}-t\text{-Bu})(\text{NAr})(\text{O}-t\text{-Bu})$.

tion and the polymerization was again run for some days. Up to 10 cycles were carried out over a period of 32 days.

3. Results and discussion

3.1. Supporting material

The activity of the supported complexes heavily depends on the diols used. Fluorinated diols like 4,4'-(hexafluoroisopropylidene)-diphenol increase the activity by the factor of 4 compared with bisphenol A (Table 1). This is similar to the soluble Schrock-initiators—due to electron-withdrawing effects the hexafluoro complex $\text{Mo}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{OC}(\text{CH}_3)_2\text{CF}_3)_2$ (**1**) is several times more active than the *tert*-butyl complex $\text{Mo}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{O-}t\text{-Bu})_2$ (**3**) [1]. BET-measurements show that the specific

surface and the amount of active sites of the heterogeneous catalysts depend strongly on the amount of diols (Fig. 1). The specific surface is increased from $100 \text{ m}^2/\text{g}$ of the pure Al_2O_3 to about $260 \text{ m}^2/\text{g}$ after crosslinking the MAO.









The difference of activity in ROMP between complex (**1**) and (**2**) after immobilization was found to be very small, (**1**) shows a bit more of activity.

The size of the catalysts grain is about 5–10 μm (SEM measurements). TEM focus series on single Al_2O_3 crystals (diameter about 10–20 nm) confirm a surface layer of MAO and diols with a thickness of 2–10 nm.

3.2. Heterogenization of complexes

The used carrier was originally developed for the immobilization of metallocenes [4]. Whereas

Table 2
Comparison of content of *cis* vinylene (σ_c) in polymers obtained by homogeneous and immobilized complex (**1**)

monomer	σ_c homogeneous [%]	σ_c immobilized [%]
	15	90
	15	60
	55	50
		50
	90	45
	95	50
	95	30
	95	0

MAO there also works as a cocatalyst, in this application MAO is just used for supporting.

Due to the fact that the amount of carbenes on the surface is rather low and remains air- and moisture-sensitive after immobilization, detailed investigations of the kind of surface-bonding

turned out to be rather difficult. Therefore experiments of solid state NMR, FT-IR spectroscopy and X-ray photoelectron spectroscopy (XPS) have not delivered satisfying proof yet.

From activity measurements and comparison of the two different complexes we suggest that

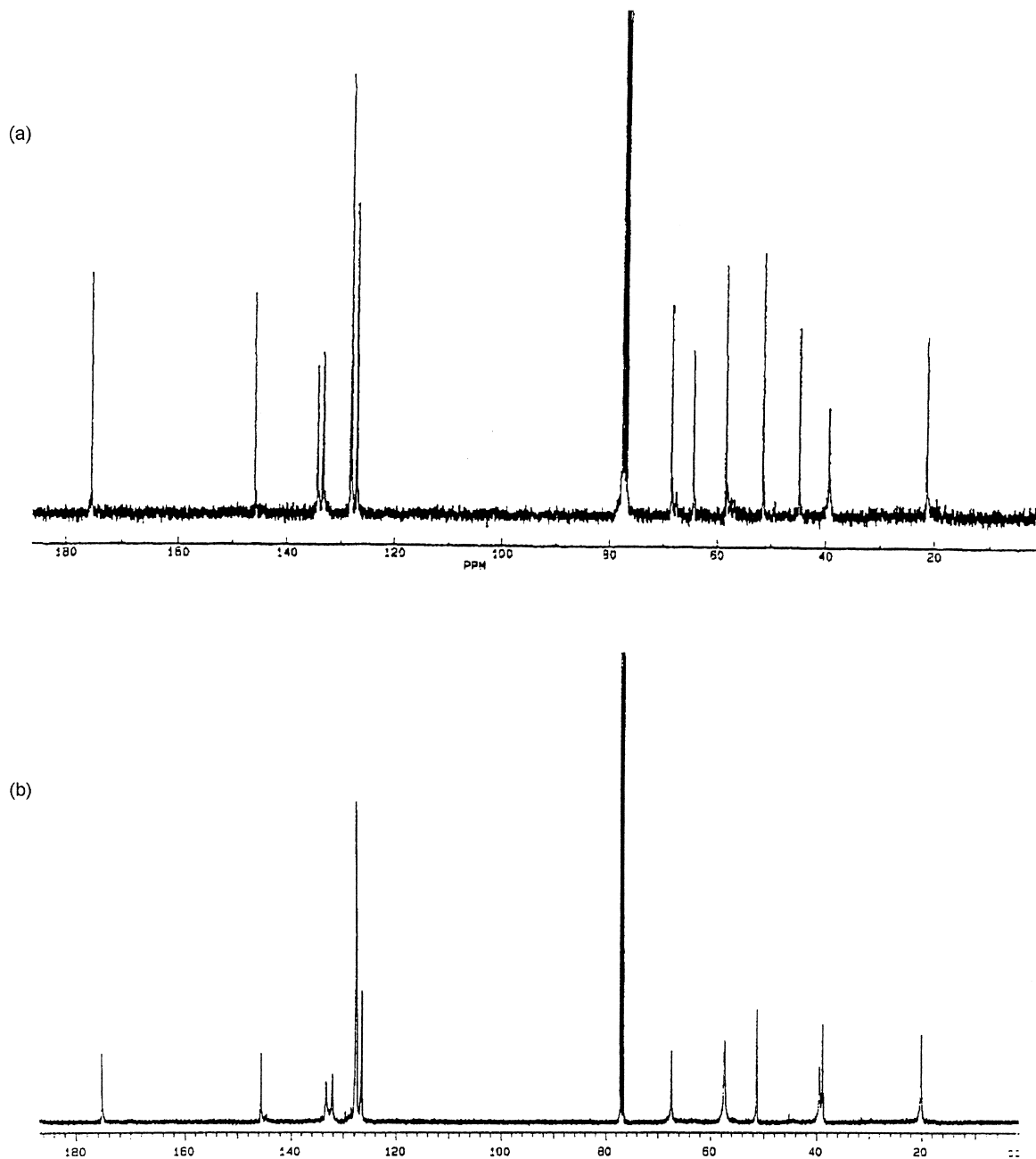


Fig. 3. 300 MHz ^{13}C NMR spectra of poly(methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate) (a) initiated by immobilized (I); (b) for comparison initiated by dissolved (I).

during immobilization an exchange of the alkoxide ligands takes place (Scheme 1). To verify this the exchange reaction was investigated by means of $^1\text{H-NMR}$ measurements. When $\text{Al}(\text{O-}i\text{-Bu})_3$ was added to a solution of the catalyst precursor (2) the same carbene signal was observed as with initiator (3) (Fig. 2). The assumed mechanism was confirmed by the influence of electron-withdrawing substituents of used diols. Furthermore the only possibility to detach the complex again from the carrier was a reaction with soluble lithium alkoxides. Those solutions could be used for new polymerization. We assume that the activation of the inactive complex (2) during immobilization can be attributed to an exchange of triflate with one hydroxy group of the diols.

It can be stated that the use of diols has two advantages: on the one hand they increase the surface of the carrier, on the other hand they provide immobilization of the complexes by exchange of ligands.

3.3. Stereochemistry of polymers

Investigations on the stereochemistry of the ROMP reaction were made by $^{13}\text{C-NMR}$ and $^1\text{H-NMR}$ in CDCl_3 . The content of *cis* double bonds of the polymers were compared between

heterogeneous and homogeneous polymerization with (1) (Table 2). In homogeneous solution complex (1) normally gives a high content of *cis* polymer because of mainly *syn* initiation species [1,10]. Due to sterical reasons differences were observed after immobilization, especially when bulky monomers were polymerized.

Norbornene or norbornadiene showed no differences ($\sigma_c = 50\%$), whereas already with dicyclopentadiene the content of *cis* vinylene decreased from 90% (homogeneous) to 45% (heterogeneous).

Cyclooctene and 1,5-cyclooctadiene were found to have a much higher *cis* content when heterogeneous initiators were used (60% and 90% *cis*). Due to back-biting and reassembling of the alkylidene groups homogeneous polymerization gave only about 15% of *cis* [11]. Heterogenization seems to prevent the polymer chains from this polymer decomposition, especially concerning 1,5-cyclooctadiene.

2-norbornenylacetate showed a *cis* content of 50% by ROMP with immobilized catalysts compared to 95% in solution [12]. Using more bulky disubstituted monomers like *endo,endo*-5,6-bicyclo[2.2.1]hept-5-ene-2-ylidibenzoate the *cis* content decreased to only 30%.

An outstanding result was obtained by polymerization of methyl-*N*-(1-phenylethyl)-2-

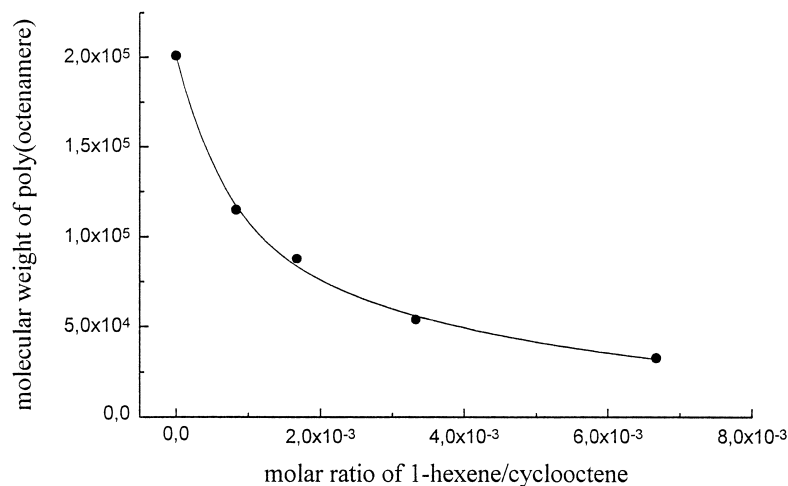


Fig. 4. Regulation of molecular weight with 1-hexene.

azabicyclo[2.2.1]hept-5-ene-3-carboxylate. This monomer containing nitrogen can be synthesized with a very high enantiomeric excess and therefore NMR studies are quite expressive. Polymerization with (1) dissolved in chlorobenzene gave a content of *cis* vinylene of 95% [13]. Surprisingly immobilized complexes produced an all *trans* polymer (Fig. 3). ¹H-COSY showed that the polymer is isotactic [14,15]. This extremely high stereoregularity was not only assumed to be the result of sterical hindrance but also of an interaction between the monomer containing nitrogen and the carrier with MAO. With this monomer no differences in stereochemistry were found with immobilized complex (1) and (2). This fact again supported the assumption that during heterogenization an exchange of the triflate or the alkoxide ligand takes place.

3.4. Regulation of molecular weight

Terminal olefins like 1-hexene could be used as chain transfer agents and thus the regulation of molecular weight was possible (Fig. 4).

Due to the fact that ROMP is a living polymerization, after polymerization the active carbenes are still stable. The polymer chains connected to the carbenes can be detached by reaction with terminal olefins. This provided the possibility to recycle these complexes. In combination with regulation of the molecular mass we were able to re-use these carbenes over a period of 30 days. During this time the polymer solution was removed 10 times. After this pe-

riod still 15% of the original activity were obtained.

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