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Ring opening metathesis polymerization of methyl-*N*-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate

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Abstract

Enantiomerically pure (**1**) and *racemic* (**2**) methyl-*N*-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate were found to undergo ring opening metathesis polymerization reactions employing molybdenum alkylidene initiators of the type $Mo(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$ ($Ar = 2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$; $R = C(CH_3)_3$; $C(CH_3)_2CF_3$; $CCH_3(CF_3)_2$) in various aprotic solvents. Chain transfer by terminal olefins such as 1-octene leads to a decrease in molecular weights which can be correlated to the amount of chain transfer agent added. In this way oligomers can be prepared with lower initiator consumption. The presence of alkylidene signals in the ^{1}H-NMR spectra and the possibility of chain transfer by acyclic olefins strongly confirm the assumption of a molybdenum alkylidene intermediate as a propagating species in a living polymerization. From the dramatic effect the presence of even small amounts of quinuclidine added as complexing agent has on the polymerization rate of (**1**) employing (**III**), we assume, that there is hardly any complexion of the initiator by the nitrogen of the monomer, otherwise the polymerization of (**1**) should be very slow or even impossible. The stereochemistry of the polymers can be correlated with the electron withdrawing effect of the initiator's alkoxide ligands. Fluorinated ligands at the initiator lead to polymers with increasing *cis*-vinylene content. There is no significant effect of the solvent's polarity on the stereochemistry of the resulting polymers.

Keywords: 2-Azanorbornene; Metathesis; Molybdenum alkylidene complexes; Optically active polymer

1. Introduction

Since the discovery of the olefin metathesis reaction there has been an intensive search for catalysts tolerating functionalities [1]. In contrast to the high polymerization rates observed for all-hydrocarbon monomers such as norbornene or dicyclopentadiene, the rates observed for cyclic alkenes containing nucleophilic functionalities are sometimes considerably slower or even zero due to some interaction with the electrophilic center of the metathesis catalyst. Metathesis of acyclic olefins containing functional groups has been found to give respectable conversion rates if one or more methylene groups are interposed between the double bond and the functional group [2], and now there is a wide variety of cyclic functionalized monomers that undergo metathesis reactions including anhydrides [3,4], cyclic imides [5], nitriles [6,7], esters [1,4], halogens [8,9], silanes and siloxanes [10].

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Molybdenum alkylidene complexes of the type $Mo(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$ (Ar = 2,6-C_6H_3-i-Pr_2; OR = various alkoxides and phenoxides) have proved to be useful initiators for the living ring-opening metathesis polymerization of cyclic olefins [11,12]. Many monomers containing functionalities have been polymerized successfully employing these initiators giving polymers with low polydispersities [13]. Since the metal–carbon double bonds of these initiators show electrophilic character, there is not only interaction between them and the strained double bonds of the monomers but with donor functionalities such as carbonyl groups, nitriles and amines as well. Nitrogen with its lone electron pair is a very nucleophilic atom, therefore cyclic olefins with nitrogen containing functionalities such as nitriles and amines turned out to be difficult to polymerize by ROMP. There have been some recent examples of metathesis reactions of nitrogen containing substrates [14], but polymerization of 2-azanorbornene derivatives gave only low conversion rates and small amounts of soluble polymers [15] using classic metathesis catalysts such as WCl_6/Lewis-acid systems.

In this paper we report the successful polymerization of *enantiomerically pure* and *racemic* methyl-*N*-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate which are easily available by an asymmetric Diels–Alder reaction [16]. Ring opening metathesis polymerizations employing $Mo(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$ with $R = C(CH_3)_3$, $C(CH_3)_2CF_3$, $C(CH_3)(CF_3)_2$ in various solvents lead to polymers of varying stereoregularity which can be seen as a kind of protected poly(amino acid). In contrast to proteins the hydrocarbon backbone of these polymers makes them more stable and resistant to hydrolytic agents. Olefinic bonds could be used for further derivatizing or crosslinking reactions, so the stereoregular optically active polymers could be useful compounds for analytical or chiral inducing purposes.

As observed in previous works with other monomers [17,18], the reactivity of the metal–carbon double bond towards carbon–carbon double bonds and the microstructure of the resulting polymers are extremely dependent on the nature of the alkoxide ligands.

For investigations on the stereoregularity of polymers derived from asymmetric monomers it is very helpful to use pure enantiomers because then there are only four possible regular structures which have to be identified whereas there are eight different dyad structures for polymers from *racemic* mixtures [19]. Stereochemistry of the optically active polymers can be determined by ^{13}C-NMR [20] and ^{1}H-COSY, whereas polymers obtained from *racemic* monomers are rather irregular and therefore show overlapping signals. In situ generated molybdenum–vinylalkylidene complexes can be good initiators too [21,22], so if the monomer is reactive enough, regulation of the molecular masses via chain transfer by terminal olefins should be possible. Thus, low molecular weight polymers may be produced with small amounts of initiator required. Addition of certain amounts of 1-octene to this monomer solution can reduce the polymer chain lengths from 200 down to the oligomer range [23].

Four-coordinate complexes of the type $Mo(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$ with $R = C(CH_3)_3$, $C(CH_3)_2CF_3$, $C(CH_3)(CF_3)_2$ form five-coordinate adducts upon addition of PMe_3 or quinuclidine [24]. Therefore these donor-ligands reduce the metathesis-activity of the initiators very effectively. The decrease in polymerization rate might be seen as a qualitative indication for the scale of interaction between the complexing agent and the initiator. Nucleophilic interaction of the monomer's donor-functionalities by comparison with quinuclidine is qualitatively investigated by addition of various amounts of quinuclidine to the initiator before polymerization. Even small amounts of quinuclidine added slow down the polymerization reaction of the 2-azanorbornene derivative substantially, so we assume that there can be only little interaction between the nitrogen in the fast polymerizing

monomer and the electrophilic center of the initiator.

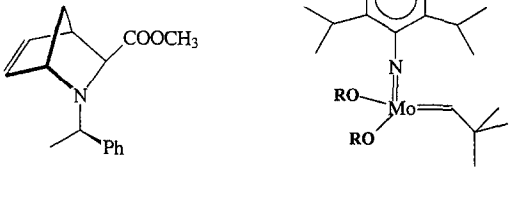
2. Results

2.1. Polymerization reaction

To our knowledge this is the first report of the successful ring opening metathesis polymerization of a 2-azanorbornene derivative using transition metal-alkylidene initiators. Methyl-*N*-(1-phenylethyl)-2-azabicyclo[2.2.1]-hept-5-ene-3-carboxylate (Scheme 1) undergoes metathesis reactions (Scheme 2) readily with each of the employed molybdenum-alkylidene initiators Mo(CH-t-Bu)(NAr)$(OR)_2$ with R = $C(CH_3)_3$ (**I**), $C(CH_3)_2CF_3$ (**II**), $C(CH_3)(CF_3)_2$ (**III**) in aprotic solvents such as benzene, chlorobenzene, dichloromethane, toluene and THF (Table 1).

Polymerizations of the pure enantiomer (**1**) and the racemate (**2**) gave full conversion with each initiator in each solvent. The polymers were isolated by precipitation from methanol.

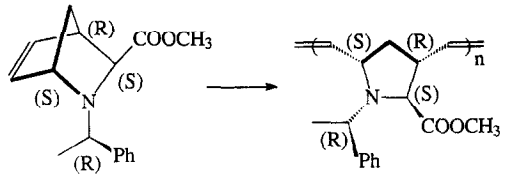
All the polymers prepared were very soluble in toluene, dichloromethane, acetone or THF, polymers having molecular weights lower than about 15×10^4 could not even be precipitated from methanol. Therefore, to avoid systematic errors due to a loss of the low molecular weight fraction, GPC measurements were done by injecting the diluted polymerization solution. Absence of the monomer signal was taken as a sign of full conversion. Increasing molecular weights can be correlated with higher ratios of monomer/initiator as is expected for a living polymerization. There were no remarkable effects of the solvent on the stereochemistry of the obtained polymers, but polymerizations occurred at lower rates in THF.



(1) pure enantiomer
(2) racemate

(I) R = Bu^t
(II) R= $C(CH_3)_2CF_3$
(III) R= $CCH_3(CF_3)_2$

Scheme 1. Monomers and employed initiators.



Scheme 2. Ring opening metathesis polymerization of (**1**).

Polymers with rather low polydispersities were obtained using (**I**) in various solvents, even though GPC measurements showed that they were strongly bimodal. Long polymerization times led to an increasing bimodality of the polymers, this was observed especially in polymerizations using initiator (**I**). The peak at high molecular weight always shows twice the molecular mass compared to the main peak. This is ascribed to a decomposition of two active centers after full consumption of the monomer, leading to a combination of two growing chains. The reasons for this are not completely clear, several possibilities have been considered in the literature [25].

Polydispersities were highest with (**III**). This initiator was the most reactive one, polymerization times were very short (< 2 min for a monomer/initiator ratio = 360 in benzene-d_6, determined by online-^{1}H-NMR) so we assume that the polymerization reaction was much faster than the first insertion step and therefore this polymerization system was not to be called really 'living' in its narrowest sense, as not all chains are started at the same time.

To obtain an overview of the rate of chain propagation relative to the initiation step the ratios of rate constants were determined by ^{1}H-NMR (Fig. 1).

Table 1
Gel permeation chromatographic analysis on poly-(1) prepared by (I), (II), (III) in various solvents

Initiator	Molar ratios of monomer to initiator	Solvent [a]	M_n found ($M_n \times 10^{-4}$ g/mol)	Polydispersity (M_w/M_n)
(I)	50	a	1.9	1.18 bimodal
(I)	100	a	3.6	1.16 bimodal
(I)	200	a	6.8	1.19 bimodal
(I)	100	b	3.8	1.15 bimodal
(I)	100	c	2.6	1.22 bimodal
(I)	100	d	2.7	1.85 bimodal
(II)	50	a	1.35	1.25
(II)	100	a	2.71	1.18
(II)	200	a	5.11	1.19 bimodal
(III)	50	a	2.2	1.26
(III)	100	a	3.0	1.44
(III)	200	a	7.4	1.45

[a] a = chlorobenzene, b = toluene, c = THF d = dichloromethane.

According to literature [26], k_p/k_i can be calculated. For given concentrations of monomer (M_0), and initiator (I_0) there is

$$M - M_0 = (1 - r)(I - I_0) + rI_0 \ln(I/I_0), \quad (1)$$

with $I \neq 0$ and $r = k_p/k_i$, M and I are the actual concentrations of monomer and initiator respectively. After polymerization of a given low quantity of monomer there is $M \rightarrow O$ and $O < I_0$ (I = concentration of unreacted initiator after full conversion of the monomer).

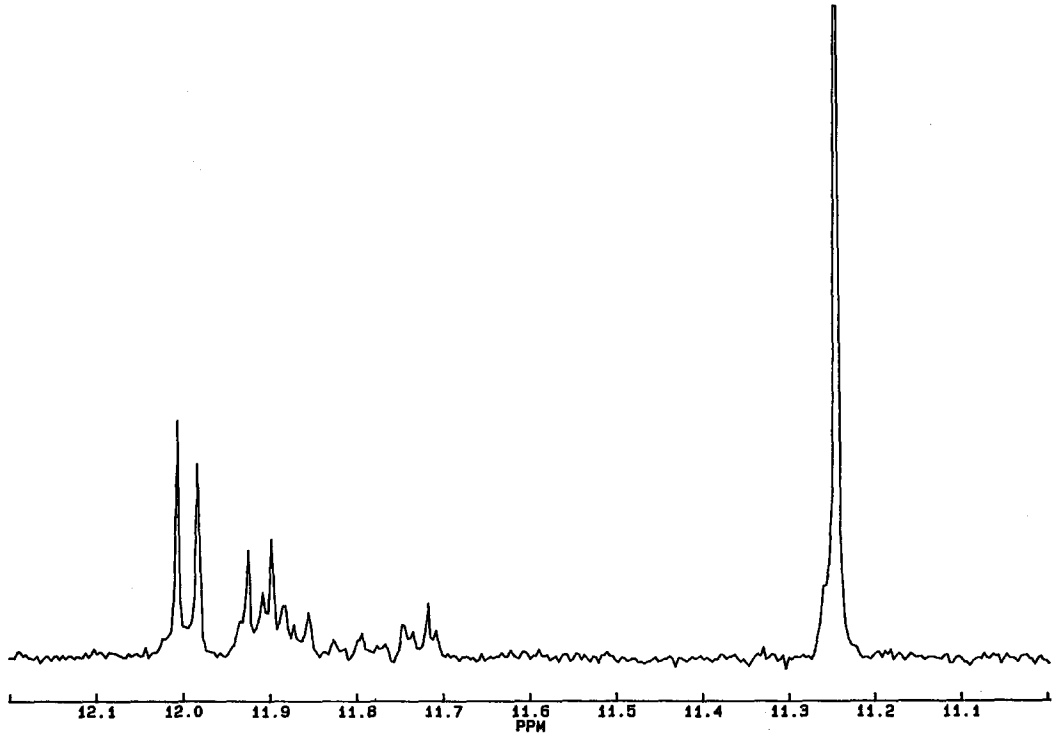


Fig. 1. Alkylidene region in 300 MHz proton NMR at the polymerization of 1 equivalent of (1) employing (I), signal of the unreacted initiator at 11.23 ppm.

Transformation of the equation above leads to:

$$k_p/k_i = (-M_0/I_0 - I/I_0 + 1) / (\ln(I/I_0) - I/I_0 + 1). \quad (2)$$

Values for k_p/k_i must be considered as rather rough estimates due to relatively low accuracy in determination of M_0/I_0 by weighing and difficult integration of the spectra, especially for the fast polymerizing initiator (**III**), but they show the clear tendency, that k_p/k_i increases with the reactivity of the initiator (**III**) > (**II**) > (**I**) (Table 2).

When polymerization of (**1**) initiated by (**III**) was carried out in presence of acyclic olefin (e.g. 1-octene) the polymers produced had significantly lower molecular weights than the polymer produced in absence of the chain transfer agent. Increasing amounts of chain transfer agent led to a decrease in molecular weights down to the oligomer range (Fig. 2).

For this investigation various amounts of 1-octene were added to the monomer solution before polymerization. The chain transfer agent/monomer ratios were varied at a constant monomer/initiator ratio. Molecular weights were determined by GPC measurement of the diluted polymerization solution.

The coherency between M_n and the monomer/initiator ratio as well as the possibility of chain transfer by acyclic olefins and the alkylidene signals in the ^{1}H-NMR spectra throughout the polymerization reaction are strong evidence for a living polymerization of (**1**) and (**2**) via formation of new molybdenum–alkylidene complexes.

Table 2
Determination of k_p/k_i at the polymerization of (**1**) by ^{1}H-NMR

Initiator	M_0/I_0	I/I_0	k_p/k_i
(**I**)	1.21	0.43	2.3
(**I**)	1.01	0.46	2
(**II**)	1.13	0.60	6.5
(**II**)	1.17	0.61	7.5
(**III**)	1.06	0.82	47
(**III**)	3.13	0.71	55

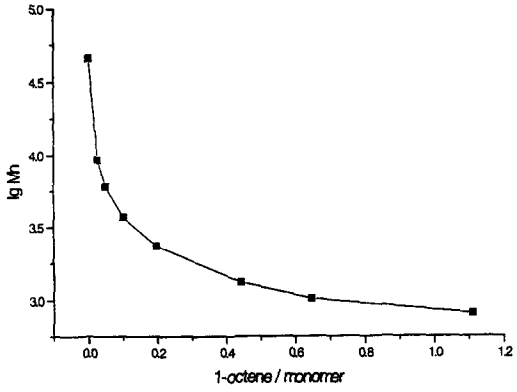


Fig. 2. Decrease of molecular weights as a function of the 1-octene/monomer ratios (monomer (**1**)/initiator (**III**) = 238).

Interaction of the electrophilic center of the initiator with free donor functionalities leads to five coordinate complexes [24] with reduced reactivity towards strained olefinic double-bonds. To understand the extent of interactions between the alkylidene complex and the tertiary amine of the monomer, the initiator (**III**) was allowed to react with several amounts of quinuclidine to give Mo(CH-t-Bu)(NAr)(OCCH$_3$(CF$_3$)$_2$)$_2$(quin) before the monomer was added. Online-NMR investigations showed that polymerization occurred at reduced rates as increasing amounts of quinuclidine were added (Fig. 3). This and the high polymerization rate of the monomer in absence

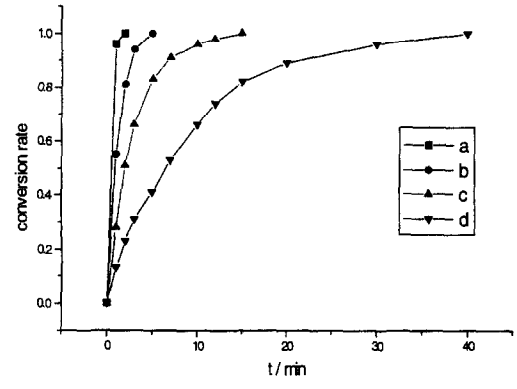


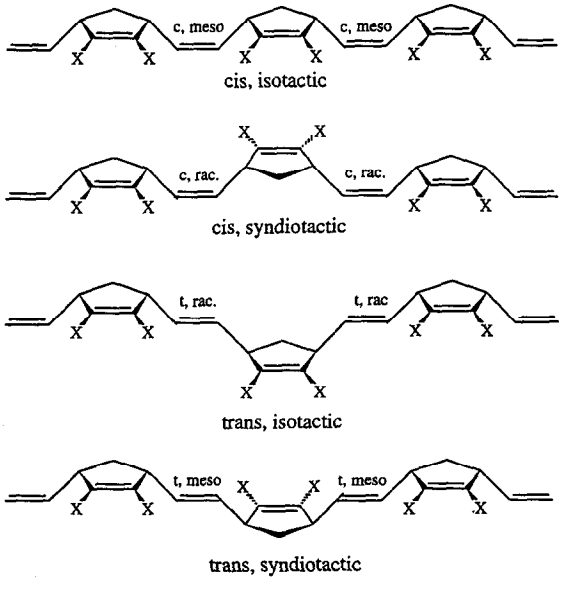
Fig. 3. Conversion rates at the polymerization of (**1**) employing (**III**) in presence of various amounts of quinuclidine at monomer (**1**)/initiator (**III**) = 100 investigated by online-NMR in benzene-d_6. (a) quin/(**III**) = 0; (b) quin/(**III**) = 1; (c) quin/(**III**) = 2; (d) quin/(**III**) = 5.

of complexing agents lead us to the conclusion that there is very little interaction between the initiator and the nucleophilic functionalities of the monomer.

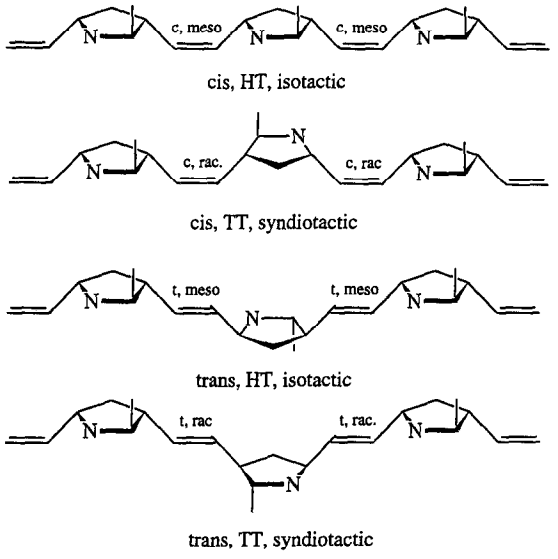
2.2. Stereochemistry of the polymers

Investigations on the stereoregularity of the polymers were made by ^{13}C-NMR in $CDCl_3$. For assignment of signals in the polymers spectra we used the notational system as for the monomer. Interpretation of the spectra is difficult, because this polymer shows different shifts for C-1, C-5 and C-6 than the other investigated polymers due to the nitrogen in position 2. Additionally, the important signals of C-1 and C-4 overlap other signals (Ph–CH–Me, respectively C7). So the only free and useful signals are (CH_3–CH) (15–22 ppm) and C-ipso (143–146 ppm), but they seem to be sensitive to *meso / racemic*-splittings rather than to *cis / trans*. Integration of the DEPT spectra of C-4 can be used only as a cross check, because there is always some distortion of the area overlapped by signals of carbons with different multiplicity.

For polymers of symmetric 2,3-disubstituted norbornadienes there are four possible regular structures (Scheme 3). The *cis*, isotactic polymers have olefinic protons, which are equivalent by virtue of a mirror plane passing through the *cis,meso* double bond. In the *cis*, syndiotactic polymer there is a C_2 axis that passes through the *cis,racemic* double bond. In both polymers a plane also passes through the methylene carbon and the midpoint of the C=C bond of each cyclopentene ring. Therefore, *cis*, highly tactic polymers with either tacticity would be expected to exhibit only one olefinic resonance. Using the same arguments on *trans*, tactic polymers one can conclude that they should also show only one olefinic resonance [27].



Scheme 3. Possible structures for tactic polymers from 2,3-disubstituted norbornadienes.



Scheme 4. Four possible regular structures for enantiomerically pure 2-azanorbornene-derivatives.

The situation becomes more difficult, as soon as nonsymmetric monomers are used, because starting from *racemic* mixtures of the monomer, there are eight possible dyad structures, whereas only four structures are possible for polymers derived from pure enantiomers.

For *cis*, tactic polymers prepared from nonsymmetric, enantiomerically pure monomers (Scheme 4) there are no mirror planes any more, the two olefinic protons are nonequivalent and therefore show two different resonances. For the *cis*, syndiotactic polymer there is still a C_2 axis passing through the midpoint

of each double bond of the polymer backbone whereas there is no symmetry operation that relates one set of equivalent olefinic protons to the other set of olefinic protons. Accordingly, the *cis*, syndiotactic polymers are expected to show two olefinic resonances related to the two sets of equivalent olefinic protons, but they should not be coupled. In the *cis*, isotactic

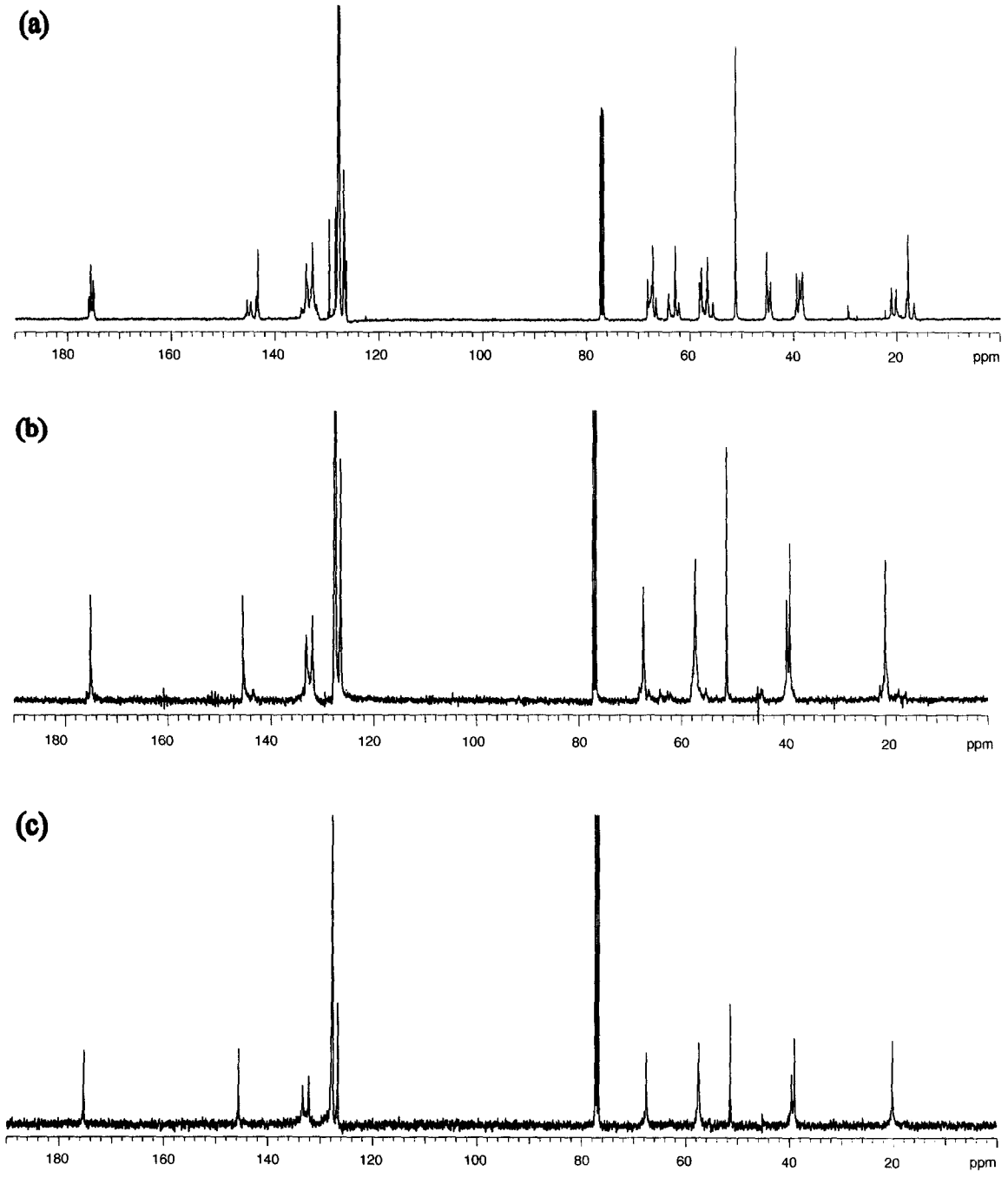


Fig. 4. 100.58 MHz ^{13}C-NMR spectra of poly-(**1**) prepared with initiator (a) (**I**), (b) (**II**), (c) (**III**).

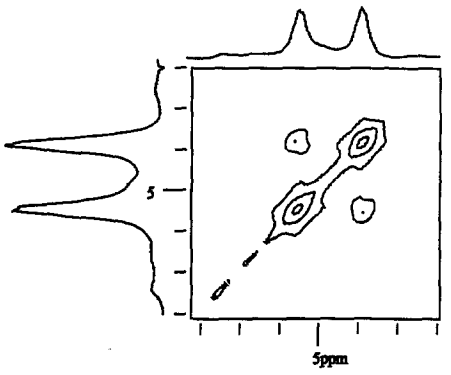


Fig. 5. 400 MHz ^{1}H COSY NMR spectrum of **P (1)/(III)**.

polymer the two nonequivalent protons are situated on one double bond and therefore should be coupled.

^{13}C spectra of polymers of (**1**) polymerized by (**III**) (**P (1)/(III)**) show a single set of lines, therefore they have to be completely stereoregular. Comparison of the C-4 resonances to those of other polynorbornenes suggests that this polymer is completely *cis* (Fig. 4c).

The ^{1}H COSY of **P (1)/(III)** (Fig. 5) shows clearly that the olefinic protons at δ 4.8 ppm and 5.1 ppm are coupled and must therefore be in an asymmetrical environment, i.e. head–tail (HT). In the ^{1}H-spectrum recorded at 200 MHz the two olefinic protons each give triplets, being coupled more or less equally to the other olefinic proton and to the adjacent proton on the ring (J about 9 Hz). Hence there is no doubt, that **P (1)/(III)** is all head–tail and, since it is made from a single enantiomer, must therefore be isotactic [28].

Table 3
^{13}C-NMR investigation on the microstructure of the polymers prepared in chlorobenzene

Initiator	Monomer	σ_c [a] (%)	Tacticity
(I)	(1)	35	Atactic
(II)	(1)	85	Mainly isotactic
(III)	(1)	> 98	> 95% isotactic
(I)	(2)	20	Atactic
(II)	(2)	70	Atactic
(III)	(2)	80	Atactic

[a] Accuracy ±5% due to overlapping signals.

P (1)/(I) and **P (1)/(II)** (Fig. 4a and 4b) are less stereoregular. **P (1)/(I)** is mainly *trans* ($\sigma_c = 0.35$), atactic and **P (1)/(II)** is mainly *cis* ($\sigma_c = 0.85$), mainly isotactic. Polymers of the racemate are atatic and show slightly higher *trans* content (Table 3).

There is no significant influence of the polymerization solvent on the stereochemistry of the polymers.

3. Experimental

3.1. Monomer synthesis

Enantiomerically pure and *racemic* methyl-*N*-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylates were synthesized by an asymmetric Diels–Alder reaction [16].

3.30 g (27.4 mmol) Methylglyoxylatehemiacetale was dissolved in 100 ml of dichloromethane with 25 g molecular sieve A3 and cooled to 0°C. Then 3.5 ml (29 mmol) R-(+)-phenylethylamine (pure enantiomer) was added dropwise and stirred at 0°C for 2 h. The mixture was cooled to −50°C and treated with 2.0 ml (26 mmol) trifluoroacetic acid and 3.20 ml (26 mmol) borontrifluoride etherate. After 10 min 2.5 ml (30 mmol) freshly cracked cyclopentadiene precooled to −30°C) were added dropwise. The reaction was quenched after 7 h by extraction with saturated sodium hydrogen carbonate solution, the organic phases were dried over sodium sulphate and solvent evaporated. The monomer was isolated by chromatography using cyclohexane/ethylacetate = 50/1 giving 4.3 g (17 mmol) as colourless oil. Recrystallization from petroleum ether gave 2.98 g (11.6 mmol) (45% relative to TFA) of methyl-*N*-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate (**1**) as white needles. mp: 45°C, $[\alpha]_D^{20} = -112.3$ (1.995, $CHCl_3$).

The *racemic* monomer (**2**) was prepared in an analogous manner: mp: 60°C ^{1}H-NMR ($CDCl_3$, 200 MHz) (**1**) δ 7.33–7.12 (5H, m, aromatics), 6.45–6.35 (1H, m, H-5), 6.30–6.20

(1H, dd, H-6), 4.31 (1H, s, H-1), 3.35 (3H, s, OCH_3), 3.03 (1H, q, Ph-CH-Me), 2.90 (1H, s, H-4), 2.21 (1H, s, H-3), 2.10 (1H, d, H-7_{anti}), 1.42 (1H, d, H-7_{syn}), 1.41 (3H, d, CH-CH_3)

^{13}C-NMR ($CDCl_3$, 50.3 MHz): 175.0 (CO), 145.2 (C-ipso), 136.7 (C-6), 133.2 (C-5), 128.9–128.2 (C-*ortho*, *meta*), 127.3 (C-*para*), 65.2 (C-3), 64.2 (Me-CH-Ph), 62.9 (C-1), 51.7 (C-4), 49.3 (OCH_3), 45.8 (C-7), 22.8 (CH-CH_3)

3.2. Polymerizations

All polymerizations were performed under nitrogen atmosphere in a dry box. Solvents (apart from benzene-d_6 and dichloromethane) were distilled from sodium/potassium alloy under nitrogen. Dichloromethane was distilled from phosphorous pentoxide under nitrogen, benzene-d_6 was passed through a column of basic alumina oxide under nitrogen.

Polymers for NMR investigations on the microstructure were prepared by addition of 200 mg of monomer dissolved in approximately 100 μl of THF, toluene or chlorobenzene to a solution of 2 mg of initiator dissolved in 100 μl of the same solvent. After 30 min polymerizations were quenched by addition of 30 μl of benzaldehyde. Polymers were precipitated from ethanol and dried in vacuum. NMR spectra were in $CDCl_3$.

For GPC measurement the calculated amount of initiator standard solution (5 mg/ml) was added to the monomer solution (100 mg/ml). After 20 min polymerizations were quenched by benzaldehyde, diluted with dry THF and directly used for measurement. Molecular weights were determined by comparison with polystyrene standards.

3.3. Polymerization of (1) in presence of chain transfer agent

100 mg (0.039 mmol) (**1**) were dissolved in the calculated amount of 1-octene standard solution containing 2.5 wt.% 1-octene in chlorobenzene. Final volumes were 1 ml by the addition of chlorobenzene; then 0.3 ml of the initiator-standard solution containing 1.15 mg (0.00163 mmol) of (**III**) was added. After 1 h polymerizations were quenched by benzaldehyde and 20 μl of the solutions were diluted with THF to 2 ml and used for GPC measurement.

3.4. Determination of the ratio of k_p to k_i

This investigation was done by integration of the alkylidene-region in the ^{1}H-NMR spectra.

Approximately 10 mg of initiator (I_0) were dissolved in benzene-d_6 and added to a solution of the calculated amount of (**1**) (M_0). After 30 min the ratio of I/I_0 was obtained by measuring the ratio of unreacted neopentylidene to total alkylidene resonances.

^{1}H-NMR ($CDCl_3$, 400 MHz), **P (1)/(III)** δ 7.1–7.3 (5H, m, aromatics), 5.2 (1H, H-5), 4.8 (1H, H-6), 4.1 (1H, H-1), 3.9 (1H, Ph-CH-Me), 3.7 (3H, OCH_3), 3.3 (1H, H-3), 2.9 (1H, H-4), 2.5 (1H, H-7_{anti}), 1.2 (3H, CH-CH_3), 1.1 (1H, H-7_{syn}) apart from aromatics, all signals appear as broad singlets.

^{13}C-NMR ($CDCl_3$, 100 MHz) **P (1)/(III)** 175.3 (CO), 145.6 (C-ipso), 133.3 (C-6), 132.2 (C-5), 127.7–127.6 (C-*ortho*, *meta*), 126.6 (C-*para*), 67.5 (C-3), 57.6 (C-1), 57.4 (Me-CH-Ph), 51.3 (OCH_3), 39.5 (C-7), 38.9 (C-4), 20.1 (CH-CH_3).

3.5. Kinetic measurement in presence of quinuclidine

In a dry box three standard solutions were prepared containing: (**a**) 5 mg (0.0071 mmol) of (**III**) in 1.00 ml benzene-d_6; (**b**) 4 mg (0.036 mmol) quinuclidine in 2 ml benzene-d_6; (**c**) 120 mg (0.466 mmol) (**1**) in 1.2 ml benzene-d_6.

The calculated amount of (**b**) was added to 110 μl of (**a**) in a 5 mm NMR tube and allowed to react for 10 min. After that 200 μl of (**c**) were injected through a septum and conversion rates were determined by online NMR at room temperature.

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References

[1] K.J. Ivin, Olefin Metathesis, Academic Press, London, 1983.
[2] (a) J.C. Mol, J. Mol. Catal., 15 (1982) 35; (b) K.B. Wagener and K. Brzezinska, Macromolecules, 24 (1991) 5273; (c) K.B. Wagener and D.W. Smith, Macromolecules, 24 (1991) 6073; (d) J.T. Patton, J.T. Boncella and K.B. Wagener, Macromolecules, 25 (1992) 3862; (e) K.B. Wagener and J.T. Patton, Macromolecules, 26 (1993) 249; (f) K.B. Wagener and Smith D.W., Macromolecules, 26 (1993) 1633.
[3] K.F. Castner, N. Calderon and J. Calderon, Mol. Catal., 16 (1982) 47.
[4] S. Matsumoto, K. Komatsu and K. Igarishi, Polym. Prep. (Am. Chem. Soc., Div. Polym. Chem.), 18 (1977) 110.
[5] J. Asrar, Macromolecules, 25 (1992) 5150.
[6] Z. Komiya and R.R. Schrock, Macromolecules, 26 (1993) 1393.
[7] M. Ungerank, B. Winkler, E. Eder and F. Steizer, Macromol. Chem. Phys., in print.
[8] W.J. Feast and B. Wilson, Polymer, 20 (1979) 1182.
[9] L.A. Shahada and W.J. Feast, Eur. Polym. J., 26 (1990) 25.
[10] K.L. Makovetsky, E.Sh. Finkel'shtein and Yu.P. Yampol'skii, Makromol.Chem., 192 (1991) 1.
[11] R.R. Schrock, Acc. Chem. Res., 23 (1990) 158.
[12] G.C. Bazan, J.H. Oskam, H. Cho, L.Y. Park and R.R. Schrock, J. Am. Chem. Soc., 113 (1991) 6899.
[13] G.C. Bazan, R.R. Schrock, H. Cho, V.C. Gibson, Macromolecules, 24 (1991) 4495.
[14] S.J. Miller and R.H. Grubbs, J. Am. Chem. Soc., 117 (1995) 5855.
[15] N. Watkins, P. Quigley, M. Orton, Macromol. Chem. Phys., 195 (1994) 1147.
[16] L. Stella and H. Abraham, Tetrahedron Lett., 31 (1990) 2603.
[17] W.J. Feast, V.C. Gibson and E.L. Marshall, J. Chem. Soc., Chem. Commun., (1992) 1157.
[18] T. Sunaga, K.J. Ivin, E., G. Hofmeister, J.H. Oskam and R.R. Schrock, Macromolecules, 27 (1994) 4043.
[19] K.J. Ivin, H.T. Ho and J.J. Rooney, Makromol. Chem., 183 (1982) 1629.
[20] (a) K.J. Ivin, G. Lapienis and J.J. Rooney, Polymer, 21 (1980) 436; (b) K.J. Ivin, G. Lapienis and C. D. Stewart, J. Mol. Cat., 8 (1980) 203; (d) K.J. Ivin, L.M. Lam and J.J. Rooney, Macromol. Chem., 195 (1994) 1189.
[21] R. Schlund, R.R. Schrock and W.E. Crowe, J. Am. Chem. Soc., 111 (1989) 4413.
[22] W.E. Crowe, J.P. Mitchell, V.C. Gibson and R.R. Schrock, Macromolecules, Comm. 23 (1990) 3536.
[23] B. Bell, J.G. Hamilton, O.N.D. Mackey and J.J. Rooney, J. Mol. Cat., 77 (1992) 61.
[24] R.R. Schrock, W.E. Crowe, G.C. Bazan, M. DiMare, M.B. O'Regan and M.H. Schofield, Organometallics, 10 (1991) 1832.
[25] W.J. Feast, V.C. Gibson, E. Khosravi, E.L. Marshall and J.P. Mitchell, Polymer, 33 (1992) 872.
[26] (a) G.C. Bazan, E. Koshravi, R.R. Schrock, W.J. Feast, V.C. Gibson, M.B. O'Regan, J.K. Thomas and W.M. Davis, J. Am. Chem. Soc., 112 (1990) 8378; (b) L. Gold, J. Chem. Phys., 28 (1958) 91; (c) P. Remp and E.W. Merrill, Polymer Synthesis, Hutenig and Wepf, New York, 1986; (d) W.J. Feast, V.C. Gibson, K.J. Ivin, A.M. Kenwright and E. Khosravi, J. Mol. Cat., 90 (1994) 87.
[27] R. O'Dell, D.H. McConville, G.E. Hofmeister and R.R. Schrock, J. Am. Chem. Soc., 116 (1994) 3414.
[28] K.J. Ivin, personal communication.