



Benchmarking of ruthenium initiators for the ROMP of a norbornenedicarboxylic acid ester

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Abstract

The kinetic study of ring-opening metathesis polymerization (ROMP) of a diester functionalised norbornene derivative, (\pm)-*exo,endo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid diethyl ester, with a series of ruthenium benzylidene complexes revealed the applicability of these initiators for well defined polymerization reactions. Values for the rate of initiation as well as the rate of propagation of the initiators were determined and correlated to the molecular weight and polydispersity of the isolated polymers. As the only initiator providing an entry to virtually monodisperse polymers the classical “first generation Grubbs-catalyst” was identified, while *N*-heterocyclic carbene based initiators polymerized with a rate of propagation much higher than the rate of initiation yielding polymers with a broader molecular weight distribution.

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1. Introduction

The perfect initiator for the ring-opening metathesis polymerization (ROMP) shows high activity, provides complete initiation, performs reactions in a stereocontrolled manner, has a broad functional group tolerance, is stable towards air and moisture and is switchable (starts the polymerization after a certain event). Within the last few years great progress was made in every special matter. With the advancement of ruthenium-based “second generation” metathesis initiators containing *N*-heterocyclic carbenes (NHC) as co-ligands the activity of ruthenium-based systems

is even higher than in molybdenum-based systems. Moreover Ru-initiators exhibit higher functional group tolerance [1,2]. Various air and moisture stable systems [2,3], as well as thermally switchable catalysts have been reported [4]. Nevertheless, there is a substantial lack of information concerning the suitability for well defined ROMP of recently introduced ruthenium-alkylidene-complexes, mainly because research in this area focuses on ring closing metathesis (RCM) [2] and only a few reports on ROMP utilizing these new initiators have been published [1,5–9]. The applicability of ruthenium initiator systems for ROMP, with emphasis on the activity is the main objective of the present study. As a simple model for a whole group of monomers with mesogenic side-groups, which are under investigation in our laboratory [10–12] a diester functionalised norbornene derivative is employed.

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2. Experimental

2.1. General

The average molecular weights and the polydispersity were determined by gel permeation chromatography with THF as the solvent using the following arrangement: Merck Hitachi L6000 pump, separation columns of Polymer Standards Service, 8 × 300 m STV 5 μm grade size (10⁶, 10⁴, and 10³ Å); refractive index detector from Wyatt Technology, model Optilab DSP Interferometric Refractometer; polystyrene standards purchased from Polymer Standard Service were used for calibration.

Infrared (IR) spectra were recorded on a Perkin-Elmer spectrophotometer with a DTGS detector, ν_{\max} in cm⁻¹. Bands are characterized as strong (s), medium (m) and weak (w).

Arrayed ¹H NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer operating at 499.803 MHz. ¹³C NMR spectra were recorded on a Varian GEMINI 200 MHz spectrometer operating at 50.286 MHz, respectively, and were referenced to SiMe₄.

2.2. Reagents

Initiators **1** and **3** were purchased from STREM and were used as received. **2** [3], **4** [3], and **7** [13] were prepared according to the literature. The initiators **5** and **6** were obtained from Ciba Specialty Chemicals. All other compounds were obtained from commercial sources and used without purification. For the reaction of initiators **1** and **3** the solvents were treated as follows: Benzene-d₆ was distilled from Na under Ar and stored over activated molecular sieves and CDCl₃ was degassed and stored over molecular sieves in a nitrogen atmosphere. Dichloromethane was dried over CaH₂ and toluene was distilled from Na/K under N₂.

2.3. General polymerization procedure in the NMR-tube using initiators **1** and **3**

Procedures were carried out in inert atmosphere. Complex **1** or **3** (0.0105 mmol, 1.0 eq.) was weighed into a small vial containing Si(SiMe₃)₄ (0.0026 mmol, 0.25 eq.) as the internal standard for the integration.

The solvent (benzene-d₆ or CDCl₃, 0.5 ml) was used to transfer the contents into a NMR-tube, which was fitted with a screw cap containing a rubber septum and taped caps. The resulting solution was allowed to equilibrate in the NMR probe at the desired reaction temperature. The monomer **7** (0.2098 mmol, 20 eq.) was diluted with 0.2 ml solvent and injected into the NMR-tube. A ¹H NMR timing sequence was commenced immediately. The initiator's carbene peak and the monomer's olefinic signals were integrated versus the standard's singlet at 0.25 ppm. The initiation rate constants (k_i) were determined by integration of the proton signal of the catalyst's carbene (20.55 ppm for **1** and 19.13 ppm for **3**) and the resting states of propagating carbene(s) (in case of **1** as the initiator: 19.87, 19.81, 19.43, 19.40, 18.61, 18.28 ppm; and for **3** as the initiator: 18.11 and 18.16 ppm) versus the standard. The propagation rate constants (k_p) were determined by integration of the olefinic proton resonances of the monomer (at 6.1 ppm) and the polymer (at 5.3 ppm).

2.4. General polymerization procedure in the NMR-tube using initiators **2**, **4**, **5**, and **6**

Procedures were carried out in ambient conditions! Complex **2**, **4**, **5** or **6** (0.0105 mmol, 1.0 eq.) was dissolved in 0.5 ml reagent-grade, non-degassed benzene-d₆ or CDCl₃. A 0.25 eq. of Si(SiMe₃)₄ were added. The resulting solution was allowed to equilibrate in the NMR probe at the desired reaction temperature. The monomer **7** (0.2098 mmol, 20 eq.) was diluted with 0.2 ml reagent-grade deuterated solvent and transferred into the NMR-tube with a pipette. The acquisition procedure and determination method for k_p were the same as outlined in Section 2.3. The initiation rate constants (k_i) were determined by integration of the H_α resonance of the catalyst's carbene (17.31 (d) ppm for **2**, 16.50 ppm for **4**, 18.55 (d) ppm for **5**, and 18.16 ppm for **6**) and the resting state(s) of propagating carbene(s) (in case of **2** as the initiator: 18.60, 18.28 ppm; for **4**: 18.13 ppm; for **5**: 18.10 ppm; for **6**: 18.38 ppm) versus the standard.

2.5. General polymerization procedure using initiators **1** and **3**

Procedures were carried out in inert atmosphere. To the monomer **7** (1.259 mmol, 300 eq.) diluted in 0.5 ml

toluene or CH_2Cl_2 , initiator **1** or **3** (0.0042 mmol, 1.0 eq.) dissolved in 0.5 ml solvent was added. The gas-tight reaction vessel was closed and transferred from the dry box to an oven and kept at the desired temperature (20, 40, or 60 °C) until the reaction was complete. The polymerization can be monitored by TLC ($R_f = 0.55$ of the monomer **7**; cyclohexane:ethyl acetate = 5:1). The polymerization was quenched by adding some drops of ethyl vinyl ether. After 30 min the solution was added dropwise to stirred methanol (50 ml). The white to rose-colored precipitate was dried under vacuum. Yields are given in Table 2. IR (NaCl, cm^{-1}): 2982 (m), 1730 (s), 1447 (w), 1380 (m), 1329 (w), 1257 (m), 1179 (s), 1097 (w), 1031 (m), 972 (w), 860 (w), 735 (w). ^1H NMR (500 MHz, CDCl_3 , 20 °C): δ 5.49–5.2 (2H, m, $\text{CH}_2=$), 4.08 (4H, q, OCH_2CH_3), 3.18–2.67 (4H, m, CH), 1.94–1.46 (2H, m, CH_2), 1.21 (6H, t, OCH_2CH_3). ^{13}C $\{^1\text{H}\}$ NMR (50 MHz, CDCl_3 , 20 °C): δ 174.1–173.1 (C=O), 133.5–130.0 ($\text{CH}_2=$), 60.8–60.6 (OCH_2CH_3), 53.1–51.9 (CH–COOEt), 47.2–39.0 (CH_2 and CH–CH=), 14.5 (OCH_2CH_3).

2.6. General polymerization procedure using initiators **2**, **4**, **5**, and **6**

Procedures were carried out in ambient conditions! The initiator **2**, **4**, **5**, or **6** (0.0042 mmol, 1.0 eq.) dissolved in 0.5 ml reagent-grade toluene or CH_2Cl_2 and added to a monomer solution of **7** (1.259 mmol, 300 eq.) in 0.5 ml of the corresponding solvent. The reaction mixture was kept at the desired temperature (20, 40, 60, 80 or 100 °C) in a drying oven until the reaction was complete. The polymerization was quenched by adding some drops of ethyl vinyl ether. After 30 min the solution was added drop wise to stirred methanol (50 ml). The brown precipitate was dried under vacuum. Yields are given in Table 2.

3. Results and discussion

3.1. Activity of the different initiators

Initiators **1–6** were used to start the ROMP of (\pm)-*exo,endo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid diethyl ester (**7**). The conversion of monomer

was monitored over time using arrayed ^1H NMR spectroscopy (cf. Table 1). The polymerization reactions exhibited clean first-order kinetics. The decrease of the initiator was also monitored as a function of time. In this case, first-order kinetics could be assumed for at least the first three half-lives. Different solvents (benzene- d_6 and CDCl_3) and temperatures (ranging from 20 to 100 °C) were employed. In case of air-stable initiators (**2**, **4**, **5** and **6**) all experiments were carried out under ambient conditions, to demonstrate, that air exclusion is not a prerequisite for the propagation of the reaction.

In benzene- d_6 as solvent, the activity of initiators at ambient temperature increases in the order $\mathbf{5} = \mathbf{6} \ll \mathbf{1} \leq \mathbf{2} < \mathbf{3} < \mathbf{4}$. Initiator **4** yields complete conversion of **7** at 20 °C in less than 1 min, while **3** requires 9 min. Initiators **1** and **2** are considerably less active than the *N,N*-bis(mesityl)4,5-dihydroimidazol-2-ylidene (H_2IMes) substituted compounds. Both accomplish virtually complete conversion after 420 min. Upon heating, the activity of **1** is enhanced. The same accounts but to a smaller extent for the activity of **2**. Switching from benzene- d_6 to CDCl_3 as the solvent, the activity of the initiators increases in the order of $\mathbf{2} < \mathbf{1} < \mathbf{3} < \mathbf{4}$ (cf. Fig. 1). Except for initiator **1**, the polymerization rates are higher in benzene- d_6 than in CDCl_3 (Scheme 1).

Finally, **5** and **6** give no observable conversion at room temperature. They are designed to start the polymerization reaction after thermal induction [4]. For **5** the temperature has to be higher than for **6** in order to get ROMP of **7**. At 40 °C, **5** gave only a conversion of 3% after 150 min, while **6** promoted the polymerization towards a conversion of 67% after the same time. In the latter case the conversion reached a plateau (Fig. 2). This observation is best explained by a gradual decomposition of **6**. Indeed the disappearance of the carbene peak of **6** in the ^1H NMR spectrum proceeded without apparent increase of the signal of resting state of the propagating carbene. The half-lives (under ambient conditions) of **6** is 3 h at 40 °C, and 45 min at 100 °C, while the half-life of **5** is 10 h at 60 °C. Decomposition of all other initiators during the polymerization plays a minor role, no adverse effects on the polymerization were observed. Both initiators **5** and **6** showed good polymerization rates at temperatures higher than 80 °C.

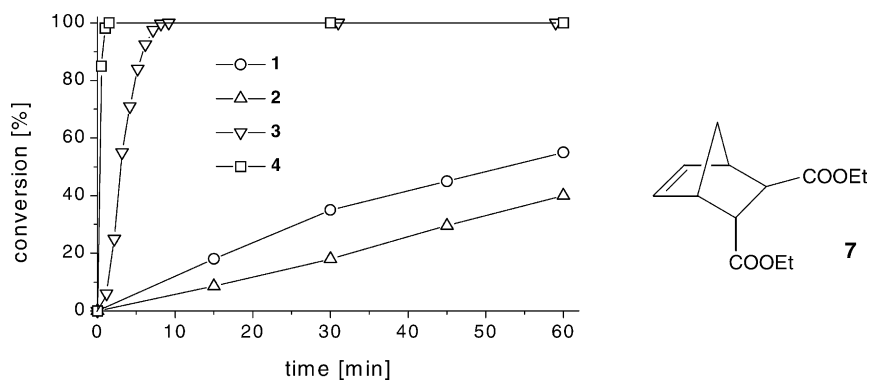
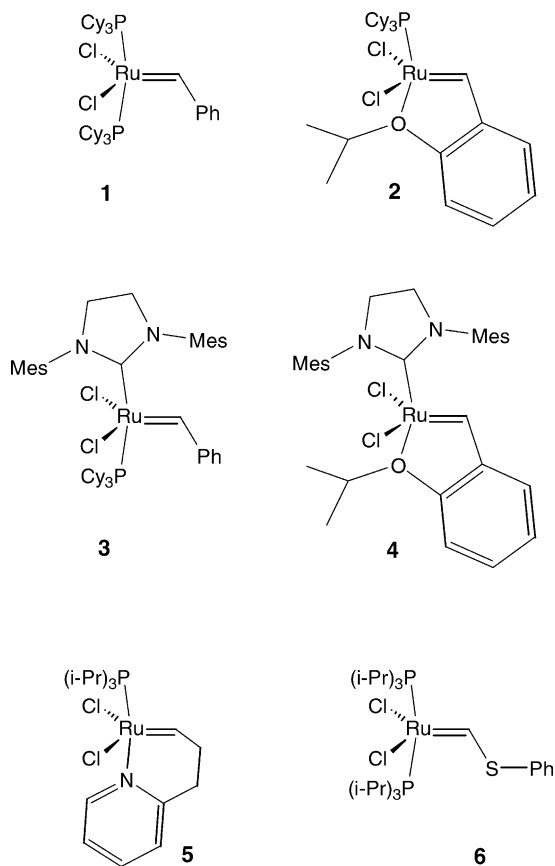


Fig. 1. Conversions of ROMP of **7** as function of time for the different initiators **1**, **2**, **3**, and **4**. Reaction conditions: 20 °C [monomer]/[initiator] = 20/1, [initiator]₀ = 0.0105 mmol, solvent: CDCl₃. Conversions determined by ¹H NMR spectroscopy. **5** and **6** showed no observable conversion.



Scheme 1. Initiators under investigation.

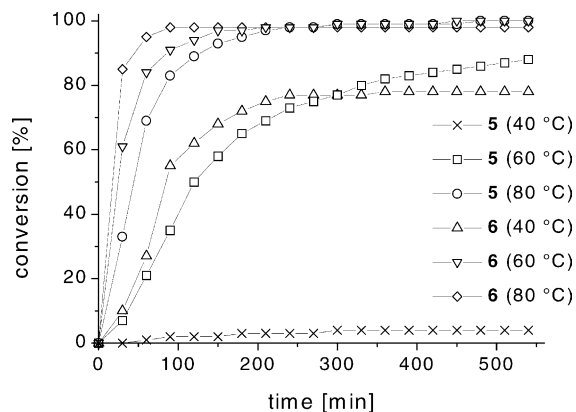


Fig. 2. ROMP of **7** using initiators **5** and **6**. Reaction conditions: 20 °C, [monomer]₀/[initiator]₀ = 20/1, [initiator]₀ = 0.0105 mmol, solvent: benzene-d₆ or toluene-d₈. Conversions determined by ¹H NMR spectroscopy.

3.2. Initiation and propagation rate constants for the initiators

To gain more information, the initiation rate constants (k_i) and the propagation rate constants (k_p) of the reactions were determined. Table 1 summarizes the obtained results. The k_i/k_p ratios clearly reveal that only initiator **1** provides a faster initiation compared to the propagation. In all other cases the k_i/k_p ratios are smaller than 1, which is indicative for a faster propagation compared to the initiation. Analyzing the initiation rates for complexes **1–4**, it is noteworthy, that the k_i for the initiation with **4** surpasses that with **3** by

Table 1

Kinetic data for the ROMP of **7** using initiators **1**, **2**, **3**, **4**, **5**, and **6**—NMR-tube experiments

Entry	Initiator	Temperature (°C)	Solvent	Time (min)	k_i ($\times 10^{-3}$) ($1 \text{ mol}^{-1} \text{ s}^{-1}$)	k_p ($\times 10^{-3}$) ($1 \text{ mol}^{-1} \text{ s}^{-1}$)	k_i/k_p
1.1	1	20	CDCl ₃	300	3.90	0.34	11.5
1.2	1	20	Benzene-d ₆	420	0.57	0.23	2.4
1.3	1	40	Benzene-d ₆	90	4.10	1.60	2.5
1.4	1	60	Benzene-d ₆	12	32.9	11.8	2.8
1.5	2	20	CDCl ₃	480	0.06	0.12	0.5
1.6	2	20	Benzene-d ₆	420	0.04	0.33	0.1
1.7	2	40	Benzene-d ₆	200	0.21	1.0	0.2
1.8	2	60	Benzene-d ₆	45	1.10	3.1	0.3
1.9	2	80	Benzene-d ₆	10	3.30	12.6	0.3
1.10	3	20	CDCl ₃	15	0.17	4.7	0.04
1.11	3	20	Benzene-d ₆	9	0.52	10.5	0.05
1.12	4	20	CDCl ₃	7	2.60	11.2	0.23
1.13	4	20	Benzene-d ₆	<1	>10.0	>67	≈0.15
1.14	5	40	Benzene-d ₆	150 ^a	n.d. ^b	n.d. ^b	n.d. ^b
1.15	5	60	Benzene-d ₆	540 ^c	≈0.004	0.07	≈0.06
1.16	5	80	Toluene-d ₈	540	≈0.005	0.20	≈0.03
1.17	5	100	Toluene-d ₈	120	≈0.010	1.1	≈0.01
1.18	6	40	Benzene-d ₆	270 ^d	n.d. ^b	n.d. ^b	n.d. ^b
1.19	6	60	Benzene-d ₆	260	≈0.011	0.29	≈0.04
1.20	6	80	Toluene-d ₈	180	≈0.088	0.67	≈0.13
1.21	6	100	Toluene-d ₈	30	≈0.90	3.16	≈0.28

Reaction conditions: [initiator]₀ = 0.0105 mmol; [monomer]₀/[initiator]₀ = 20/1; time for a conversion higher than 98% (as seen by ¹H NMR spectroscopy).

^a Conversion 3%.

^b n.d. means not determined.

^c Conversion 85%.

^d Conversion 78%.

the factor 10–20 (depending on the employed solvent), while the k_i for initiating with **2** is more than one-order of magnitude lower than the k_i for **1**. Initiation rate constants (in $1 \text{ mol}^{-1} \text{ s}^{-1}$) at 20 °C in benzene-d₆ in order of increasing values are 0.04×10^{-3} (for **2**), 0.52×10^{-3} (for **3**), 0.57×10^{-3} (for **1**) and $>10 \times 10^{-3}$ (for **4**).

These big differences in k_i can be best explained by the different electronic properties of the PCy₃ and NHC-ligand. Due to the excellent electron-donating ability of the NHC ligands, a σ -donor ligand in *trans* position should be labilized. Thus in **4**, the ether is a better leaving group despite the chelate effect compared to the PCy₃ ligand. This is supported by Grubbs and co-workers [14] who reported a decrease in the phosphine exchange rate of over two-orders of magnitude by substitution of one PCy₃ of **1** by a NHC-ligand,

i.e. complex **3**. By comparison, the chemistry is reversed with the PCy₃ ligand stabilized complexes **1** and **2**. The chelated ether ligand is a worse leaving group compared to the second coordinated PCy₃ ligand. For **2**, the effect of chelation is obvious from the finding, that the enhancement of k_i upon heating is distinctly less pronounced compared to **1**. For **3** and **4** this comparison is not possible because of the fastness of the reaction. The high k_i found for the reaction with **1** in CDCl₃ can be explained by an enhanced solvation of the intermediate $14 e^-$ species and the liberated phosphine [14]. In general, the k_i values for initiation with **5** and **6** are very small compared to the initiators **1–4**. It has to be noted, that the accuracy of the initiation rate constants for **5** and **6** is of poor quality compared to those for **1** and **2**, because of a low initiation. Also for **3** and **4** the accurate determination

of k_i is difficult. The main reasons for uncertainties arise from the low percentage of initiation, the very fast polymerization reaction, and that mixing is not instantaneous and approximately 40 s are necessary to obtain the first ^1H NMR spectrum.

3.3. Polymers prepared with the initiators 1–6

For further assessment of the applicability of the initiators 1–6 for ROMP, we prepared polymers from 7 using reaction conditions based on the NMR experiments presented above. A 0.33 mol% of the initiator was used to polymerize 7 in 1 ml solvent. Again, only the ROMP reactions with 1 and 3 were carried out in inert atmosphere. The polymerization was fol-

lowed by TLC and quenched after the disappearance of the monomer spot by adding 50 μl of vinyl ethyl ether. Precipitation and reprecipitation in methanol and drying in vacuum gave poly7. The polymers were characterized by means of ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR and IR spectroscopy as well as GPC. Table 2 summarizes the results and compares them with the k_i/k_p ratios obtained from the NMR measurements. Initiator 1 yielded nearly monodisperse poly7 (M_w/M_n ratios close to 1) with a molecular weight close to the calculated value and high polymer yields, but was comparably slow. 2 appeared to be a less attractive initiator for ROMP of 7, because the PDIs were higher and the polymer was harder to purify resulting in lower yields. 3 provided a distinctly faster polymerization reaction,

Table 2
ROMP of 7 using initiators 1, 2, 3, 4, 5, and 6—lab scale preparation of poly7

Entry	Initiator	Temperature ($^{\circ}\text{C}$)	Solvent	Time (h)	Yield	M_n^a	M_w/M_n^a	Cis-content (%) ^b
2.1	1	20	CH_2Cl_2	24	92	73460	1.08	20
2.2	1	20	Toluene	24	98	82550	1.08	20
2.3	1	40	Toluene	5	98	75830	1.06	20
2.4	1	60	Toluene	3.5	95	66000	1.04	20
2.5	2	20	CH_2Cl_2	24	92	139760	1.5	20
2.6	2	20	Toluene	24	73 ^c	115600	1.3	20
2.7	2	40	Toluene	6.5	75 ^c	113650	1.3	20
2.8	2	60	Toluene	4	83 ^d	112650	1.3	20
2.9	2	80	Toluene	2	81 ^d	117240	1.3	20
2.10	3	20	CH_2Cl_2	1	90	673860	1.7	65
2.11	3	20	Toluene	1	93	687680	2.4	65
2.12	3	40	Toluene	1	94	375850	2.1	65
2.13	3	60	Toluene	0.5	91	402640	2.1	65
2.14	4	20	CH_2Cl_2	4	94	192730	1.5	65
2.15	4	20	Toluene	4	94	185710	1.4	65
2.16	4	40	Toluene	1	92	213250	1.6	65
2.17	4	60	Toluene	1	95	157490	1.5	65
2.18	5	40	Toluene	24	17	325210	2.8	20
2.19	5	60	Toluene	24	30	433600	3.5	20
2.20	5	80	Toluene	24	46	230790	3.7	20
2.21	5	100	Toluene	24	88	363870	3.7	20
2.22	6	40	Toluene	24	73	186570	2.2	20
2.23	6	60	Toluene	24	79	197970	2.1	20
2.24	6	80	Toluene	24	86	175100	2.3	20
2.25	6	100	Toluene	24	98	128920	2.0	20

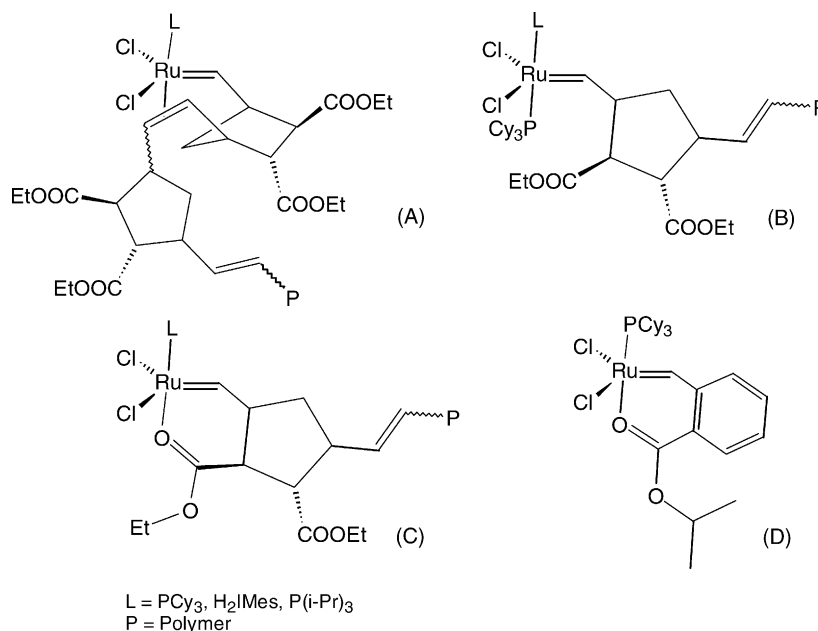
Reaction conditions: $[\text{monomer}]_0 = 1.26 \text{ mmol}$; $[\text{monomer}]_0/[\text{initiator}]_0 = 300/1$.

^a Polydispersity determined by GPC in THF and reported relative to polystyrene standards ($M_{\text{calc}} = 71,500$).

^b Determined by ^1H NMR.

^c Reprecipitated three times from CH_2Cl_2 /methanol.

^d Reprecipitated twice from CH_2Cl_2 /methanol.



Scheme 2. Presumable resting states of the propagating polymer chain (A–C) and an ester-stabilized Ru-benzylidene (D).

at the expense of a high PDI and a low initiation, being responsible for the high molecular weight of the polymer. Initiator **4** combined high activity and air-stability with lower molecular weights and high yields. Furthermore, the PDIs of the polymers prepared with **4** are low compared to those synthesized with **3**. From that **4** is in all points superior to **3**. Finally, **5** and **6** give rather broad molecular weight distributions but good yields at reaction temperatures higher than 100 °C (Table 2).

Consequently **1** is the initiator of choice when a narrow molecular weight distribution of the polymer is desired. Otherwise **4** is the most potent initiator combining air-stability and high activity in producing satisfyingly defined polymers. If it is important to utilize a switchable initiator, **5** should be preferred rather than **6**. This statement is based on the finding, that only **5** starts the polymerization at temperatures higher than 40 °C (cf. Fig. 2). The ^1H and ^{13}C NMR spectra of the polymers were in agreement with the structures proposed and showed a generally similar pattern of chemical shifts and intensities. Initiators **1**, **2**, **5**, and **6** produce polymers with predominantly *trans*-double bonds ($80 \pm 7\%$ *trans*-content), while in poly**7** prepared with the NHC stabilized initiators **3** and **4** more *cis*-vinylene units are present ($65 \pm 7\%$ *cis*-content).

These values neither change within the error margins by using different reaction temperatures, nor by variation of the solvent. The stereochemistry was determined by integration of appropriate signals in the ^1H NMR spectra. As determined by TOCSY-NMR spectroscopy, the peak at 5.52 ppm was used to quantify the *trans*-double bond amount, while the peak at 5.20 ppm is indicative for a *cis*-geometry. Values were checked by evaluation of the ^{13}C NMR spectra according to the literature [15–17].

3.4. Environmental stability of the propagating chains

The structure of the resting state is crucial for understanding the environmental stability of the propagating polymer chains.

Analysis of the ^1H NMR spectra for the kinetic studies discussed previously revealed several carbene signals for the “resting states” of the propagating polymer-chains. At least three different resting states (and their stereoisomers) can be attributed to these signals. Various possibilities for the formation of resting states are possible. As shown in Scheme 2 (A) the coordination of the newly formed double bond, (B)

the recoordination of the released phosphine (only in case of **1** and **3**), or (**C**) the coordination of one of the ester substituents are arguable: According to Chen and co-workers, a probable resting state can be formed by double bond coordination [18]. The latter statement was corroborated by electrospray ionisation tandem mass spectrometry [19]. A widely accepted dormant species results from the recoordination of a released phosphine [14]. Moreover, Fürstner et al. showed that the ester functionality in the benzylidene complex (**D**) is able to coordinate to the ruthenium center forming a six-membered ring related to the chelation by the ether group in initiators **2** and **4**. Complex **D** is air-stable [20]. Thus, we assume that the ester-groups in **7** might be responsible for the environmental stability of the propagating carbenes. Some insight into the structure of the propagating carbenes is delivered by the carbene peaks observed in the ^1H NMR spectra during the kinetic investigations: For the polymerization of **7** by **1** at 20°C six different carbene peaks at 18.27, 18.60, 19.39, 19.43, 19.81, and 19.87 ppm were detected in benzene- d_6 . At elevated temperatures (60°C) only a single carbene, giving a peak at 18.27 ppm is dominant. In CDCl_3 , peaks at 18.52 and 18.71 ppm were observed. With initiator **2** at ambient reaction conditions two carbene signals were located at 18.27 and 18.60 ppm in benzene- d_6 (for CDCl_3 : 18.52 and 18.71 ppm). Moreover, the carbene peak in the ^1H NMR of compound **D** was observed as a doublet at 18.76 ppm (in CD_2Cl_2) [20]. Therefore we assigned these carbene-peaks to resting states related to **C** and the signals in the range from 19.39 to 19.87 ppm to resting states like **B**. In consequence, NMR-data corroborate the presence of resting states of the propagating carbenes of type **C**, stabilizing the growing chain against decomposition by oxygen. Further work concerning this topic is currently ongoing in our laboratories.

4. Conclusion

The comparison of the six different initiator systems reveals a preference for **1** when a narrow molecular weight distribution of the polymer is desired. Compound **4** is the initiator of choice, if exclusion of air should be avoided. Moreover **4** is the most potent initiator, showing the highest activity, but at the ex-

pense of a somewhat broader molecular weight distribution of the resulting polymer. To make use of a thermally switchable initiator, **5** should be employed, as the starting temperature for the ROMP reaction has to be higher than for **6**. Initiators **2**, **4**, **5**, and **6** facilitate the ROMP of **7** in environmental conditions, thus exclusion of oxygen is not a prerequisite for the preparation of poly**7**.

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