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Journal Name

ARTICLE

Reactivity of norbornene esters in ring-opening metathesis polymerization initiated by a N-chelating Hoveyda II type catalyst

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S.A. Kiselev,[a] D.A. Lenev[b], A.A. Lyapkov[a], S.V. Semakin[b], G. Bozhenkova,[a] F. Verpoort[a,d*] and R.V. Ashirov[a,c*]

The reactivity and activation parameters for the ring-opening metathesis polymerization of eight norbornene esters in the presence of a N-chelating Hoveyda-Grubbs II type catalyst were determined using in situ ^{1}H-NMR. The ester molecules differ in the structure of substituent and the location of ester groups. Kinetic studies have shown that effective polymerization constants and activation parameters highly depend on the monomer structures. It was demonstrated that the elongation of the aliphatic chain does not significantly affect the reactivity of the ester, but has a high impact on the activation parameters of the reaction. Branching the aliphatic substituent has a significant influence on the reactivity and activation parameters. Furthermore, the orientation of the ester substituents in the norbornene ring substantially affects the activation parameters.

Introduction

The ring-opening metathesis polymerization (ROMP) has become a powerful method for producing side-chain-functionalized polymers.[1-2] The high tolerance of ruthenium-based catalysts to a range of functional groups[3] allowed to obtain functionalized norbornene-based polymers for different purposes.[4-7] In particular, many efforts have recently been dedicated to study norbornene esters as possible raw material for ROMP polymer preparation. Norbornene esters are already utilized in industry to prepare functionalized polymers useful in the production of adhesives, as well as in the manufacturing of decorative, isolation and electrical products.[8-10] One of the most attractive methods for preparing ROMP polymers from norbornene esters is reaction injection molding (RIM). This method has already proven itself for the production of thermoset polymers from dicyclopentadiene (DCPD).[11-14] Polymerization rate is a crucial parameter of the RIM process, and generally the rate should be considerably high. Therefore the kinetic studies of the polymerization should give fundamental information for carrying out the RIM process of norbornene esters via ROMP.

It is known that ROMP kinetics strongly depends on structures of the monomer and catalyst.[15] In this study we investigated ROMP of eight of norbornene-2,3-dicarboxylic acid esters in the presence of a N-chelating Hoveyda II type catalyst by means of ^{1}H-NMR *in-situ* (fig.1). These esters are valuable as possible raw materials for the production of new ROMP polymers with new properties. There are two main factors affecting the polymerization rate. The first factor is the orientation of the ester substituents in the norbornene ring. This factor has been previously investigated using three ester stereoisomers of norbornene-2,3-dicarboxylic acid of which the following reactivity pattern was observed: exo,exo-isomer > exo,endo- > endo,endo-isomer.[16,17] The second factor is the length and branching degree of the aliphatic ester substituent, which also can affect the reactivity and activation parameters of ROMP. This second factor is of high interest because length as well as branching degree of the aliphatic substituent, affect the polymer properties. It is known that polyolefins having a

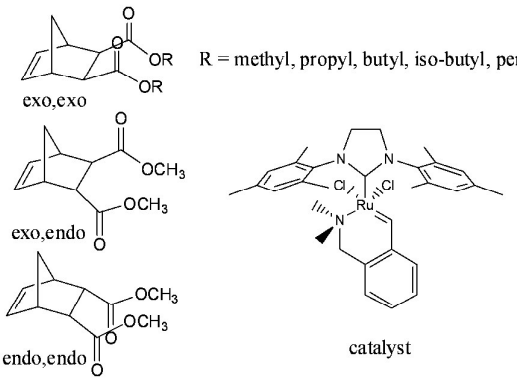

Fig.1 Monomers used in ROMP and commercial available ruthenium catalyst

[a] National Research Tomsk Polytechnic University, Tomsk, 634050, Russian Federation. Fax: +7 382 256 3304, e-mail: kiselevstani@gmail.com
[b] Limited Liability Company "NIOST" Tomsk, 634067, Russian Federation. Fax: +7 382 270 2332, e-mail: lda@niost.ru
[c] National Research Tomsk State University, Tomsk, 634050, Russian Federation.
[d] Laboratory of Organometallics, Catalysis and Ordered Materials, State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China.
[e] Fax: +7 382 278 3726, e-mail: KiselevStani@gmail.com

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short pendant group behave as thermoplastics, whereas polyolefins with a long pendant group act as elastomers. Although the reaction conditions used in this study are different from the RIM conditions having insight in the impact of these two factors is essential. All of the presented monomers are available in industrial scale and can be easily obtained from DCPD and corresponding esters.

Experimental

Chemicals

To obtain the exo,exo norbornene esters the corresponding anhydride of exo,exo-2,3-norbornenedicarboxylic acid and alcohol were used.[19] The anhydride of endo,endo-2,3-norbornenedicarboxylic and methanol were used to synthesize the dimethyl ester of endo,endo-2,3-norbornenedicarboxylic acid. The dimethyl ester of exo,endo-2,3-norbornenedicarboxylic acid was obtained using DCPD and dimethylfumarate.[18] For the polymerization procedure a N-chelating Hoveyda II type catalyst - (1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)-dichloro(o-N,N-dimethylamino-methylphenylmethylene) ruthenium was used as initiator. The catalyst (**1**) was synthesized according to the patent literature.[19]

Characterization

NMR spectra were collected on the Bruker Avance III 400 MHz spectrometer in $CDCl_3$ at the room temperature. Chemical shifts were assigned using the residual proton resonance of the deuterated chloroform. The purity of the esters, ranging from 97.5 to 99.0 %, was determined from ^{1}H-NMR spectral data.

Catalyst (**1**):

^{1}H-NMR: 1.87 (s, 6H), 2.54 (s, 12H), 4.08 (s, 6H), 6.66 (d, 1H, J=7.3 Hz), 6.94 (d, 1H, J=7.3 Hz), 7.03 (s, 4H), 7.10 (t, 1H, J=7.3 Hz), 7.46 (t, 1H, J=7.3 Hz), 18.69 (s, 1H).

^{13}C-NMR: 19.1 (C13), 21.2 (C12), 47.8 (C9), 51.5 (C11, C11'), 65.9 (C8), 127.2 (C6), 128.6 (C5), 128.7 (C4), 129.5 (16), 130.8 (C3), 133.6 (C7), 134.2 (C15) 138.1 (15), 138.7 (14), 148.3 (C2), 213.8 (C10), 313.9 (C1).

Exo,exo-dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**2**):

^{1}H-NMR: 1.49 (m 1H, C7Hα, 3J=1.7 Hz, 2J=9.3 Hz), 2.10 (d 1H, C7Hβ, 2J=9.3 Hz), 2.61 (d, 2H, C2H, C3H, 3J=1.9 Hz), 3.08 (m, 2H, C1H, C4H), 3.65 (p, 2H, C9H3, C11H3), 6.20 (m, 2H, C5H, C6H, 3J=1.8 Hz).

Exo,endo-dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**3**)

^{1}H-NMR: 1.45 (d, 1H, C7Hα, 2J=8.8 Hz), 1.61 (d, 1H, C7Hβ, 2J=8.8 Hz), 2.68 (m, 1H, C3H, 3J=4.5 Hz, 3J=1.6 Hz), 3.12 (bs, 1H ,C4H), 3.26 (bs, 1H, C1H), 3.37 (m, 1H, C2H, 3J=4.5 Hz), 3.64 (s, 3H, C9H3), 3.71 (s 3H, C11H3), 6.06 (dd, 1H, C6H, 3J=5.6 Hz, 3J=2.8 Hz), 6.27 (dd, 1H, C5H, 3J=5.6 Hz, 3J=3.2 Hz).

Endo,endo-dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**4**)

^{1}H-NMR: 1.31 (d 1H, C7Hα, 2J = 8.6 Hz), 1.46 (m, 1H, C7Hβ, 3J=1.84 Hz, 2J=8.6 Hz), 3.15 (m, 2H, C1H, C4H), 3.28 (d, 2H, C2H, C3H, 3J=1.7 Hz, 3J=1.35 Hz), 3.60 (p, 2H, C9H3, C11H3), 6.25 (m, 2H, C5H, C6H).

Exo,exo-dipropyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**5**)

^{1}H-NMR: 0.92 (t, 6H, C11H3, C15H3, 3J=7.4 Hz), 1.49 (d, 1H, C7Hα, 2J=8.8 Hz), 1.61 (s, 4H, C10H2, C14H2, 3J=7.4 Hz), 2.12 (d, 1H, C7Hβ, 2J=8.8 Hz), 2.60 c. (2H, C2H, C3H), 3.07 (bs, 2H, C1H, C4H), 4.0 (m, 4H, C9H2, C13H2), 6.20 (s, 2H, C5H, C6H).

Exo,exo-dibutyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**6**)

^{1}H-NMR: 0.92 (t, 6H, C12H3, C17H3, 3J=7.2 Hz), 1.35 (m, 4H, C11H2,C16H2, 3J=7.2 Hz), 1.48 (d, 1H C7Hα, 2J=9.2 Hz), 1.58 (p, 4H, C10H2, C15H2, 3J=7.2 Hz), 2.12 (d, 1H, C7Hβ, 2J=9.2 Hz), 2.59 (s, 2H, C2H, C3H), 3.07 (bs, 2H, C1H, C4H), 4.01 (m, 4H, C9H2, C14H2), 6.20 (s, 2H, C5H, C6H).

Exo,exo-diisobutyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**7**)

^{1}H-NMR: 0.91 (d, 12H, C11H3, C12H3, C16H3, C17H3, 3J=6.8 Hz), 1.48 (d, 1H, C7Hα, 2J=9.2 Hz), 1.87 (m, 4H, C10H2, C15H2, 3J=6.8 Hz), 2.13 (d, 1H, C7 Hβ, 2J=9.2 Hz), 2.62 (d, 2H, C2H, C3H), 3.08 (bs, 2H C1H, C4H), 3.71-3.89 (m, 4H, C9H2, C14H2), 6.20 (s, 2H, C5H, C6H).

Exo,exo-dipentyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**8**)

^{1}H-NMR: 0.85 (t, 6H, C13H3, C19H3, 3J=7.2 Hz), 1.27 (m, 8H, C12H2, C11H2, C17H2, C18H2), 1.43 (d, 1H C7Hα, 2J=9.1 Hz), 1.56 (m, 4H, C10H2, C16H2), 2.09 (d, 1H, C7Hβ, 2J=9.1 Hz), 2.55 (s, 2H, C2H, C3H), 3.03 (bs, 2H, C1H, C4H), 3.98 (m, 4H, C9H2, C15H2), 6.16 (s, 2H, C5H, C6H).

Exo,exo-dioctyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**9**)

^{1}H-NMR: 0.87 (t, 6H, C16H3, C25H3, 3J=7.0 Hz), 1.25-1.60 (m, 20H, C11-C15H10, C20-C24H10), 1.47 (d, 1H C7Hα, 2J=9.2 Hz), 1.59 (m, 4H, C10H2, C19H2), 2.12 (d, 1H, C7Hβ, 2J=9.2 Hz), 2.59 (s, 2H, C2H, C3H),3.07 (bs, 2H, C1H, C4H), 4.02 (m, 4H, C9H2, C18H2), 6.20 (s, 2H, C5H, C6H).

ROMP kinetics procedure

All manipulations were carried out in air. Polymerizations were performed in NMR tubes. 0.3 ml solution in $CDCl_3$ of the monomer and catalyst were prepared with the required concentration and heated at the desirable temperature followed by mixing and transferring the mixture into the NMR tube. The NMR tube was shaken and transferred into the NMR-spectrometer and heated at the desirable temperature. Monomer concentration in the resulting solution was ranging from 0.3 to 0.65 mol/L. Catalyst concentration was 20 times less than monomer concentration for monomers **2**, **5**-**9** and in 300 times less for monomers **2**-**3**.

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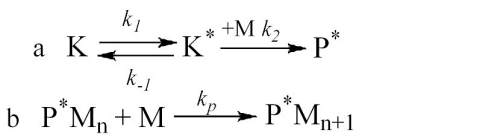
The monomer conversion was measured by comparing the signal from double bond of the norbornene ring (6.0-6.5 ppm) to the signal from the double bond of the polymer (5.0-5.5 ppm). The catalyst concentration was measured by comparing the signal from the catalyst 6.66 (ppm) to the signal from residual proton resonance of deuterated chloroform (7.26 ppm).



Scheme 1 Initiation (a) and propagation (b) steps of the polymerization.

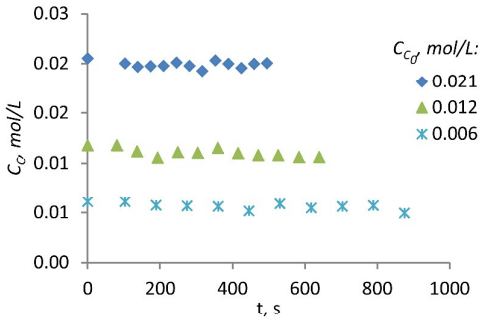


Fig. 2 Catalyst concentration variation during polymerization of **2** for different initial concentrations of catalyst (C_{M_0} = 0,35 mol/L, 50 °C)

Results and discussion

A method of comparison of reactivity and activation parameters

The first coordination of the monomer to the ruthenium complex **1** initiates the polymerization and at the same time activates the catalyst. It is well documented that the Hoveyda-Grubbs catalysts have two different activation mechanisms.[15,20-23] However, sterically hindered olefins are capable of activating Hoveyda-Grubbs catalyst only through a dissociative mechanism (scheme 1 a).[15]

As a consequence, the initiation rate is equal to the formation rate of active centers P^*. During the polymerization process the catalyst concentration changes insignificantly; its decline is about 1 % of the initial amount of the initiator (fig. 2). Furthermore, despite the excess of the catalyst used the resulting polymers display high molecular weights (Tab. 1). Based on the data represented in fig. 1 and in table 1 it can be concluded that the initiation rate is slower than the propagation rate. This conclusion is confirmed by the ratio of the constants k_i/k_p determined for different N-chelating ruthenium catalysts. [24,25] Dissociation of the N-chelating ligand from the ruthenium center of **1** generates a 14-electron species C^* that is more active than the 16-electron complex **1**, denoted as C for the kinetics (fig. 3). Therefore, the rate-determing step of the initiation stage is the nitrogen dissociation having a constant k_1. Since the monomer is not involved at this stage, the rate of the initiation stage only depends on the catalyst concentration and temperature. Therefore, the monomer has an influence only on the initiation constant k_2 and the propagation constant k_p (scheme 1b).

The kinetics of monomer consumption is complex (fig. 4 a and b). During the polymerization process the monomer is consumed in the stages of the initiation and the growth of the polymer chain.

$$-\frac{dC_M}{dt} = k_2 C_{C^*} C_M + k_P C_{P^*} C_M \qquad (1)$$

The concentrations of the 14-electron complex C_{C^*} and the active centers C_{P^*} are small. During the polymerization the number of active centers grows continuously due to the lack of chain transfer and termination reactions.[26-30] Since the constant k_1 is much smaller than the constants k_{-1} and k_2, it is feasible to apply the steady state approximation for the concentration of the 14-electron complex C_{C^*}.

$$\frac{dC_{C^*}}{dt} = k_1 C_K - k_{-1} C_{C^*} - k_2 C_{C^*} C_M = 0 \qquad (2)$$

$$C_{C^*} = \frac{k_1 C_I}{k_{-1} - k_2 C_M} \qquad (3)$$

Table 1 Molecular weight of the polymers obtained from **2**

C_{C_0}, mol/L	C_{M_0}/C_{C_0}	M_nx10^{-5}, g/mol
0,021	17	8,5
0,012	30	10,1
0,006	57	7,6

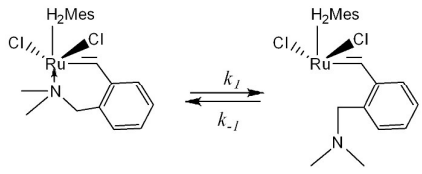


Fig. 3 The first stage of the initiation step

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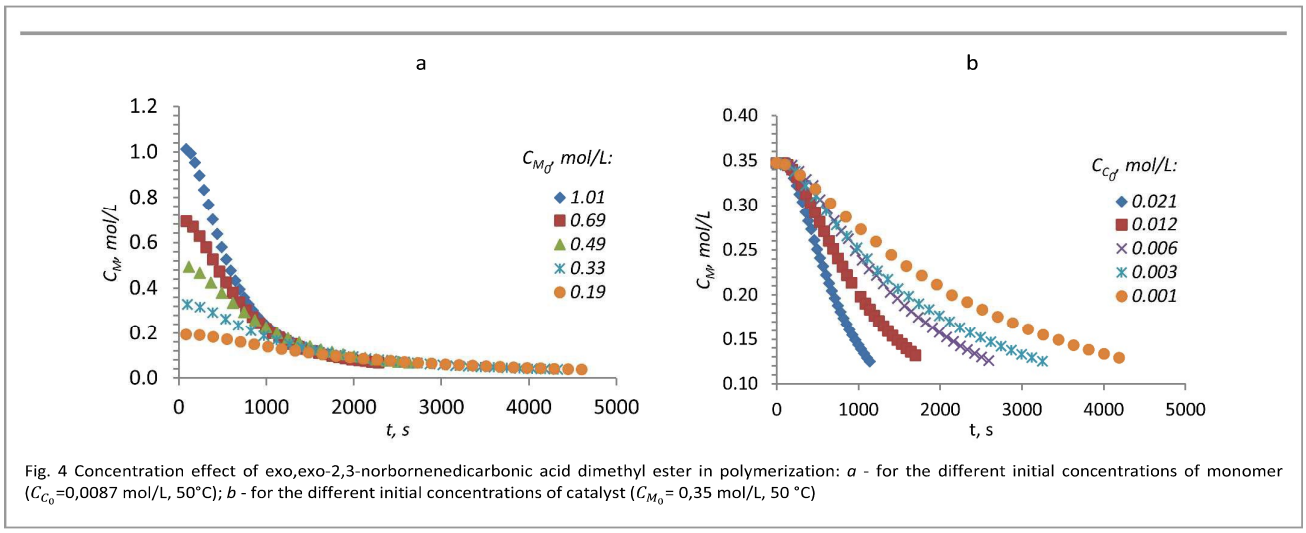

Fig. 4 Concentration effect of exo,exo-2,3-norbornenedicarbonic acid dimethyl ester in polymerization: *a* - for the different initial concentrations of monomer (C_{C_0}=0,0087 mol/L, 50°C); *b* - for the different initial concentrations of catalyst (C_{M_0}= 0,35 mol/L, 50 °C)

Since the monomer concentration is significantly higher than the 14-electron complex $C_M \gg C_{C^*}$ consequently the second stage of the initiation can be approximated as a pseudo-first order reaction, proceeding with the constant $k_{2_e} = k_2 C_{M_0}$. Since amount of the catalyst during the polymerization changes insignificantly it can be assumed that the catalyst concentration in the reaction process is equal to the initial catalyst concentration $C_C \cong C_{C_0}$. Hence, the concentration of active centers is described by equation 4.

$$\frac{dC_{P^*}}{dt} = \frac{k_1 C_{C_0}}{k_{-1} - k_2 C_{M_0}} k_2 C_{M_0}. \qquad (4)$$

After integration:

$$C_{P^*} = \frac{\frac{k_1}{k_{-1}} k_2 C_{C_0} C_{M_0}}{1 + \frac{k_2}{k_{-1}} C_{M_0}} t. \qquad (5)$$

The amount of active centers is equal to the amount of monomer, spent on the initiation. Thus, the change in monomer concentration is described by equation 6.

$$-\frac{dC_M}{dt} = \frac{\frac{k_1}{k_{-1}} k_2 C_{C_0} C_{M_0}}{1 + \frac{k_2}{k_{-1}} C_{M_0}} + \frac{\frac{k_1}{k_{-1}} k_2 C_{C_0} C_{M_0}}{1 + \frac{k_2}{k_{-1}} C_{M_0}} k_p C_M t \qquad (6)$$

The first part of the right side of the equation 6 can be

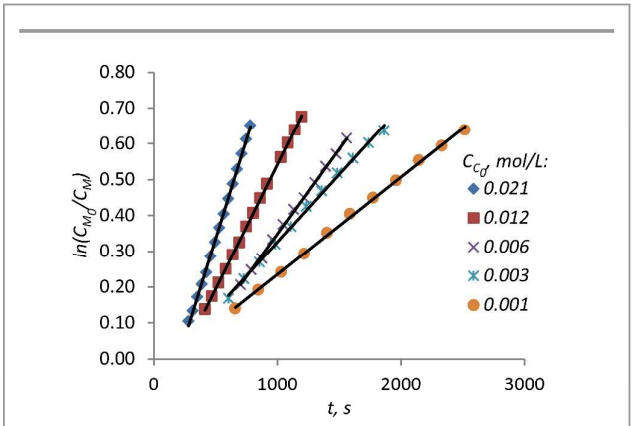

Fig. 5 Semi-log graphs of polymerization of **2** at different initial catalyst concentrations (C_{M_0}=0,35 mol/L, 50 °C)

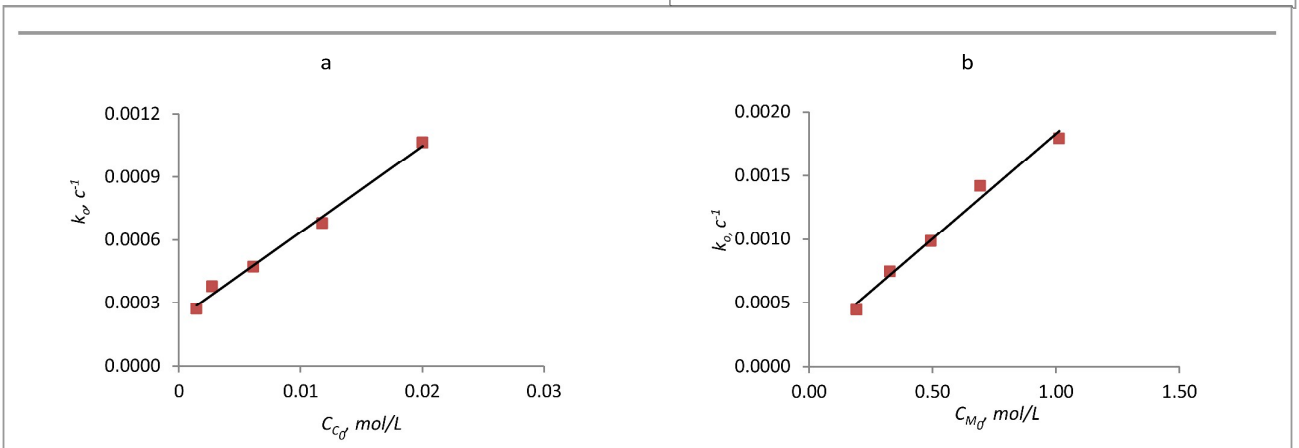

Fig. 6 Dependence of the polymerization constant k_o of **2**: *a*- at different initial concentrations of catalyst (C_{M_0}= 0,35 mol/L, 50°C); *b*- at different initial concentrations of monomer (C_{C_0}=*0,0087* mol/L, *50*°C)

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neglected because it has a much smaller contribution than the second part since a considerable consumption of monomer can be presumed. Expression $t\frac{k_1}{k_{-1}}k_2C_{C_0}C_{M_0}/(1+\frac{k_2}{k_{-1}}C_{M_0})$ can be replaced by $C_{C_0}f$, where f – is the initiation efficiency equaling to $C_{P^*}/C_{C_0}=\frac{k_1}{k_{-1}}k_2C_{M_0}t/(1+\frac{k_2}{k_{-1}}C_{M_0})$.[31] This substitution allows to simplify equation 6 into equation 7:

$$-\frac{dC_M}{C_M}=C_{C_0}fk_pdt \qquad (7)$$

After integration:

$$ln\frac{C_{M_0}}{C_M}=C_{C_0}fk_pt \qquad (8)$$

The values of f for each of monomers differ only in constant k_2 which is depending on the monomer structure. Accordingly, it is possible to use the product fk_p for comparison of reactivity and activation parameters.

The slope of the linear section on the semi-log graph is equal to the observed constant of polymerization k_o (fig. 5). Furthermore, the product of initiation efficiency and the propagation constant is equal to constant k_o divided by the initial concentration of catalyst C_{C_0}. The constant k_o linearly depends on the initial concentrations of monomer and catalyst (fig. 6). Since the initiation efficiency f is depending on the initial concentration of the monomer a linear dependence of the constant k_o *vs*. C_{M_0} is provided. The constant k_o has a linear dependence on C_{C_0} because the initial concentration of the catalyst is included in equation 8. Based on the obtained data it can be decided that the effective constant of polymerization k_e equaling to $k_o/C_{C_0}C_{M_0}$ can be used to compare the reactivity and activation parameters of the monomers.

Influence of the length and branching of the ester substituents on the reactivity and activation parameters for exo,exo-2,3-norbornenedicarbon acid esters 2-9.

The reactivity and activation parameters of the esters were compared by the constant k_e. The Arrhenuis equation was used to determine the value of the activation parameters. The graphs of dependences of lnk_e from $1/T$ are linear (fig. 7) indicating that the mechanism of interaction of the catalyst and monomer is independent from the temperature.

It was expected that the elongation of the aliphatic tail from 1 to 8 carbon atoms would lead to a gradual decline in reactivity in the series. However, from the data represented in table 2, it follows that the elongation of the aliphatic substituent affects the reactivity of esters insignificantly. In contrast, the branching of the substituent, affects the reactivity considerably. The constant k_e of ester **7** is six times less than the constant k_e of the analogous ester **6** bearing a linear butyl chain. From these data it can be suggested that branched substituents sterically hindering the coordination of the double bond from the monomer to ruthenium.

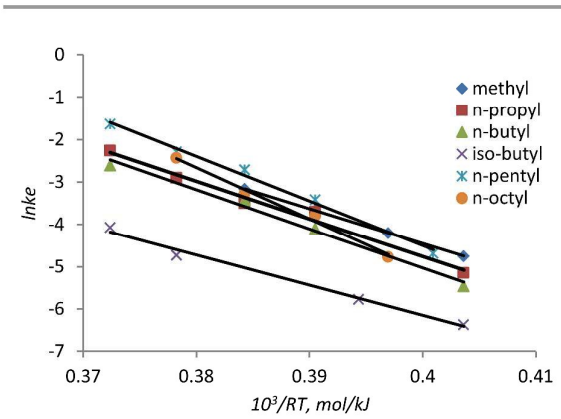

Fig. 7 Arrhenius plots for polymerization of esters **2**-**9**

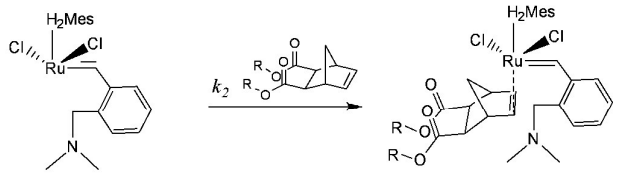

Fig. 8 The second stage of the initiation step

The data in table 2 demonstrates that elongation of aliphatic substituent increases both activation parameters. In order to understand the change in the activation parameters it is essential to understand which of the constants is affected more by the monomer structure. Constant k_e contains four constants of which constants k_1 and k_{-1} are independent from the monomer structure. The structure of monomer significantly influences on the constants k_2 and k_p. Constant k_2 characterizes the rate of addition of the monomer to the 14-electron species. In this process, the double bond of the ester molecule takes the vacant place in the coordination sphere of the ruthenium complex (fig. 8).

It is unlikely that the monomer structure influences on the rate of this process. It is more possible that the previous monomer unit prevents addition of the approaching monomer, however, this factor is not specific to this reaction

Table 2 Reactivity and activation parameters of polymerization of the esters **2**-**9**

Ester	Substituent	k_e, L mol^{-1} s^{-1} (30°C)	E_a, kJ mol^{-1}	A, L mol^{-1} s^{-1}
2	methyl	0,11	82	$2\cdot10^{12}$
5	*n*-propyl	0,10	89	$2\cdot10^{13}$
6	*n*-butyl	0,08	92	$7\cdot10^{13}$
7	*iso*-butyl	0,01	72	$6\cdot10^{9}$
8	*n*-pentyl	0,21	105	$2\cdot10^{16}$
9	*n*-octyl	0,17	121	$2\cdot10^{18}$

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stage. Most probably the monomer structure has an influence on the propagation constant k_p.

It is known that norbornene acid esters in the polymerization process are capable of chelating the active form of the ruthenium catalyst by the carbonyl oxygen of the ester group with the formation of a six-membered intramolecular complex.[32,33] Therefore, there are two active forms of the ruthenium complex which can participate in the polymer chain growth simultaneously (fig. 9).

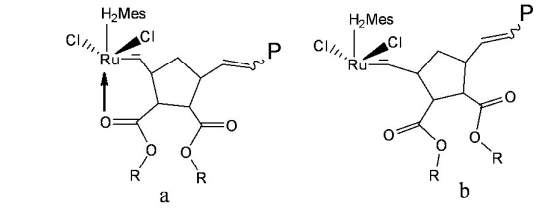

Fig. 9 Chelated (a) and non-chelated (b) forms of the active ruthenium species

The bond strength of Ru-O depends on the donor properties of the carbonyl oxygen. The elongation of aliphatic substituent enhances the donor properties of the carbonyl oxygen thereby increasing the bonding strength between the ruthenium and oxygen. In the formation of the transition state, the double bond of the monomer replaces oxygen from the coordination sphere of the ruthenium. This replacement is accompanied by the break-up of the intramolecular complex (fig. 10). In order to break the intramolecular complex it is necessary to expend some energy equalling to dissociation energy of the bond Ru-O. The elongation of aliphatic substituent making the bond Ru-O stronger increases the amount of energy required for the dissociation of Ru-O bond, and hence increasing the value of activation energy. If the activation energy corresponds to the height of the potential barrier then the pre-exponential factor can be attributed to the entropy of activation. Activation entropy change depends on the difference of the number of degrees of freedom between initial and transition states. The number of degrees of freedom of the six-membered intramolecular complex is less than the transition state. The bond strengthening of Ru-O results in a diminution of the six-membered ring mobility. Thus, the increase of pre-exponential factor can be explained by the decline of number of degrees of freedom of the intramolecular complex caused by the elongation of aliphatic substituent.

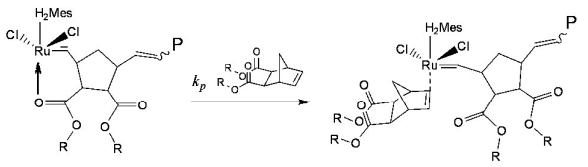

Fig. 10 Interaction of the intramolecular complex with the monomer

The carbonyl oxygen and the ruthenium have to be positioned in a certain way relative to each other in order to form a complex. Furthermore, the geometry of the molecule modifies during the formation of the bond Ru-O. One of the obstacles to form an intramolecular complex is the steric factor. Since the sterical hindering *iso*-butyl substituent cannot be located next to each other properly the carbonyl oxygen of branched ester substituent is not capable of forming a strong bond with the ruthenium. This fact reduces the value of the activation energy and the value of the pre-exponential factor. Moreover, the *iso*-butyl fragments of the previous monomer units impede the placement of the monomer in the coordination sphere of ruthenium, which also reduces the reactivity of the ester.

Influence of the position of substituents relative of norbornene ring on the reactivity and activation parameters dimethyl esters 2,3-norbornendicarbon acid

Recently, we have reported that the structure of the stereoisomers of dimethyl ester 2,3-norbornendicarbonic acid has an impact on its reactivity in ROMP (fig. 1).[17] A reactivity sequence having the highest reactivity for the exo,exo-isomer followed by the reactivity of the exo,endo-isomer and ending with the lowest reactivity for the endo,endo-isomer was observed. Whereas, with respect to the activation energy, the lowest activation energy is displayed by the endo,endo-isomer, the exo,exo-isomer has a higher and the exo,endo-isomer possesses the highest activation energy. The ester substituent in endo-position hinders the interaction of double bonds of the monomer and ruthenium carbene, thereby reducing the reactivity of the esters with the substituent in endo-position.

To compare the activation energy and pre-exponential factor the effective constant of polymerization k_e is applied. Activation parameters of monomers are different from each other (Tab.3). To explain why each monomer has different activation parameters the monomers were divided by their capability to form the intramolecular complex. The exo,endo-isomer is more capable to generate the Ru-O bond since its ester substituents are located on opposite sides with respect to the norbornene ring and do not interfere with each other when forming an intramolecular complex. For this monomer the Ru-O bond is strong and the intramolecular complex is immobile. The Ru-O bond is stronger and the intramolecular complex is rigid relative to the other isomers. Therefore, the exo,endo-isomer is characterized by high values of the activation energy and the pre-exponential factor. The exo,exo-

Table 3 Activation parameters of the stereoisomers of 2,3-norbornendicarbonic acid dimethyl ester

Isomer	E_a, *kJ mol*$^{-1}$	*A, L mol*$^{-1}$ *s*$^{-1}$
exo,exo	82	$9\ 10^{13}$
exo,endo	105	$2\ 10^{17}$
endo,endo	72	$7\ 10^{10}$

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isomer is the second isomer in terms of ability to form the bond Ru-O. This ester concedes to the exo,endo-isomer as its ester substituents are located on the same side with respect to the norbornene ring. Such location of substituents hinders the formation of the Ru-O bond. The Ru-O bond is weaker and the intramolecular complex is more labile. Therefore, in comparison with the exo,endo isomer, the exo,exo-isomer is characterized by low values of the activation energy and the pre-exponential factor.

The endo,endo-isomer is the third isomer in terms of the ability to form the Ru-O bond. Due to the location of the ester substituents inside the norbornene ring this ester is unable to form a strong Ru-O bond. The ester group in the endo-position cannot enter properly the coordination sphere of the ruthenium to form an intramolecular complex. Therefore, this molecule is characterized by low values of the activation energy and the pre-exponential factor.

Conclusion

It was demonstrated that the structure of the 2,3-norbornenedicarbonic acid esters affects their reactivity (k_e, *L mol^{-1} s^{-1}*) and activation parameters (E_a, *kJ mol^{-1}* and *A, L mol^{-1} s^{-1}*) in ROMP initiated by a N-chelating Hoveyda II type catalyst. It was determined that the elongation of the aliphatic ester substituent has no impact on the reactivity (k_e) but, however, leads to an increase of the activation parameters (E_a and *A*). The branching of the aliphatic substituent leads to a decrease of both the reactivity (k_e) and the activation parameters (E_a and *A*). Based on the values of the activation parameters it was assumed that the active ruthenium is able to form the intramolecular complex.

Furthermore, the location of the ester substituents of norbornene dicarbonic acid dimethyl ester stereoisomers affects the activation parameters (E_a and *A*), of which their values can be explained by the capability of isomers to form the intramolecular complex.

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The reactivity and activation parameters for the ROMP of eight norbornene esters in the presence of a N-chelating Hoveyda-Grubbs II type catalyst were determined. Kinetic studies prove that effective polymerization constants and activation parameters highly depend on the monomer structures.

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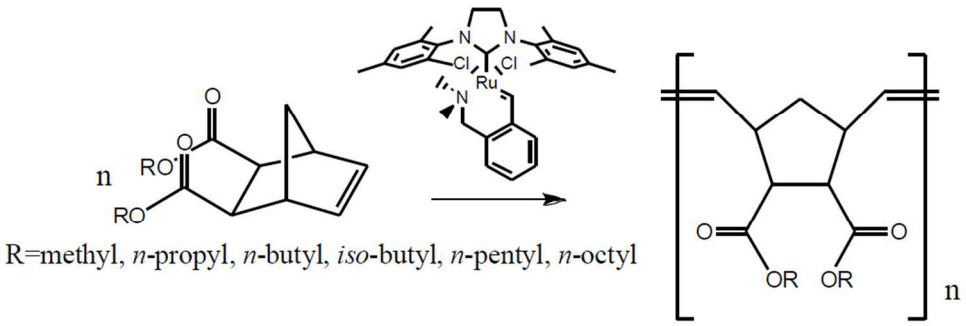

R=methyl, *n*-propyl, *n*-butyl, *iso*-butyl, *n*-pentyl, *n*-octyl

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