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Chapter 2

Ring Opening Metathesis Polymerization

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.71085

Abstract

In recent years, the olefins metathesis has established itself as a powerful tool for carbon-carbon bonds forming and has found numerous applications in polymer chemistry. One of the important directions of metathesis is the polymerization with cycle opening. A study of new ruthenium catalysts, resistant to the many functional groups effects, has showed the possibility of synthesizing functionalized polymers with unique properties. In this chapter, reactivity and activation parameters of eight different norbornene dicarboxylic acid alkyl esters in the presence of a Hoveyda-Grubbs II catalyst for the ring opening metathesis polymerization were determined by ^{1}H NMR analysis *in-situ*. The molecules of esters differ in the aliphatic radical structure and the location of the substituent groups. Kinetic studies have shown that effective polymerization constants and activation parameters strongly depend on the monomer structure. It is shown that the elongation of the aliphatic radical does not significantly affect the reactivity, but significantly changes the activation parameters. The branching of the aliphatic radical significantly affects both the reactivity of the corresponding ester and the activation parameters of the polymerization. The position of the substituents in the norbornene ring of the ester also has a significant effect on the activation parameters of metathesis polymerization.

Keywords: ring opening metathesis polymerization, nuclear magnetic resonance, dicyclopentadiene, alkyl esters of norbornene dicarboxylic acid, Hoveyda-Grubbs catalysts, observed rate constant, activation energy

1. Introduction

Ring opening metathesis polymerization (ROMP) is a process of one or more cyclic olefins transformation to polymer catalyzed by metal carbene compounds. Indeed, the number of

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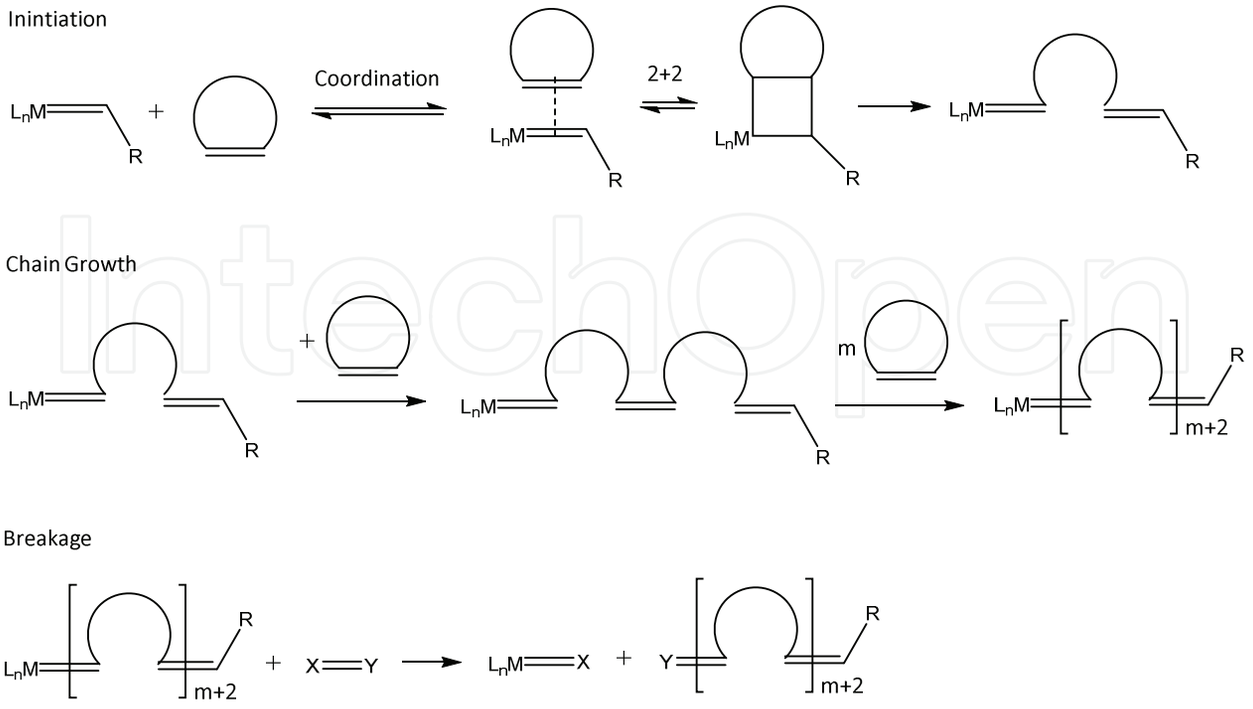
double bonds both in polymer and in monomer is equal [1–4]. As well as in any other type of polymerization, ROMP can be divided into several stages (**Scheme 1**).

The initiation begins with the coordination of the cycloolefins' double bond with the metal-carbene complex. The next step is a formation of a metal-cyclobutane intermediate. This process occurs in each act of addition of the monomer during the chain growth. The intermediate decomposes to form a new metal-carbene complex, with the growing chain being a ligand attached to the metal via a double bond.

The polymerization continues until the monomer is completely reacted or an equilibrium state is reached or the reaction is terminated by the addition of a special reagent that blocks the catalyst.

Living polymerization with ring opening metathesis is terminated by removing the transition metal from the end of the growing chain and its further deactivation. Deactivation in this case involves the formation of a complex unable to initiate polymerization [5]. Ethyl vinyl ether is an effective stopper for most ruthenium catalysts. It forms a very stable complex of the [Ru]=CHOEt type and ensures the functionalization of the polymer end-group. Acrylate derivatives of 2-butene-1,4-diol, succinic anhydride or butyl acrylate can also stop the growth of the macromolecule [6].

ROMP, as well as most metathesis reactions, is reversible, so the described transformations can proceed both in the forward and backward directions. The direction of the reaction can be predicted using the Gibbs energy:



Scheme 1. Stages of ROMP.

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$$\Delta G = -RT \cdot \ln K_{\text{равн}} = \Delta H - T \cdot \Delta S \quad (1)$$

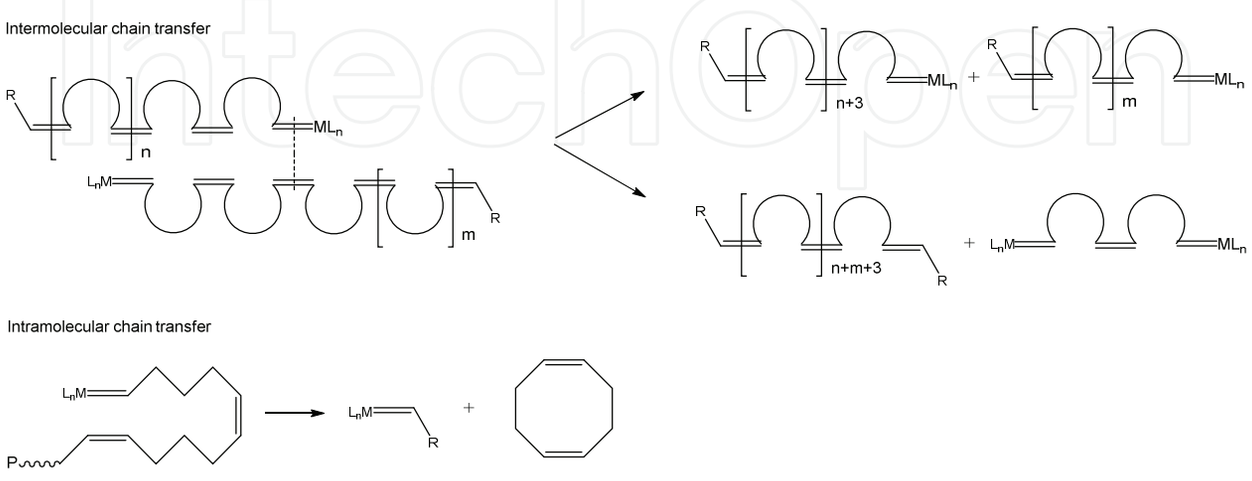
The enthalpy factor makes an essential contribution to ROMP's Gibbs energy. This fact is explained by a high strain energy of cyclic unsaturated compounds participating in the polymerization [7]. The cycle strain energy of most cycloalkenes is more than 20 kJ/mole. For example, norbornene has an energy of about 100 kJ/mole [8]. The strain energy of the cycle releasing during the decomposition of the metal-cyclobutane complex and maintaining the forward direction of the reaction. However, if the deformation energy of cycle is low, the contribution of the entropy factor into the Gibbs energy becomes more significant in comparison with a smaller enthalpy factor. In this case, the entropy factor must be properly reduced in order to implement the direct process by increasing the monomer concentration or decreasing the temperature of the process [9].

Secondary metathesis reactions can occur in addition to the main described reactions during the polymerization process. Intermolecular and intramolecular chain transfers are two main side reactions of ROMP (**Scheme 2**).

During the intermolecular transferring, the active metal-carbene complex located at the end of one macromolecule interacts with the double bond of the adjoined macromolecule, which leads to fragment exchange process. The reaction proceeds simultaneously in two directions. One of them provides two polymer chains with the active ruthenium on both. The second leads to one inactive chain and one chain with two active centers.

At the intramolecular chain transferring, the active metal-carbene complex reacts with the double bond of the same macromolecule led to a cyclization of the polymer chain. The listed side reactions, eventually, lead to a broadening of the molecular mass distribution (MMD) and a decrease in a molecular weight of the polymer [10].

The chain transfer as well as the spontaneous termination of the growing chain is highly improbable, so ROMP is a living polymerization. ROMP polymers are characterized by high molecular weights and a narrow MMD, as well as for products of other living polymerizations [11].



Scheme 2. Intermolecular and intramolecular chain transfers in ROMP.

2. Well-defined ruthenium metathesis catalysts

Up until the mid-1970s, the information about the structure of the active center of olefin metathesis catalysts was not known. Catalytic systems were mixtures of various compounds containing a transition metal. For example, in the late 1960s, Calderon and Goodyear employees published a number of papers about usage of a catalyst consisting of WCl_6, $AlEtCl_2$, and ethanol [12, 13]. Cyclic olefins form polymers (copolymers) of a high tacticity in a presence of this catalyst [14]. Catalytic systems prepared from compounds based on transition metals such as vanadium $VCl_4/Al(Hex)_3$; $V(Ac)_3/AlC1(C_2H_5)_2$; titanium $TiCl_4/Al(C_2H_5)_3$ and $TiCl_4/AlCl_3/Al(C_2H_5)_3$ [15]; molybdenum $MoCl_5/Al(C_2H_5)_3$ [16] as well as catalysts based on osmium, ruthenium, and iridium chlorides [17] were used in ROMP.

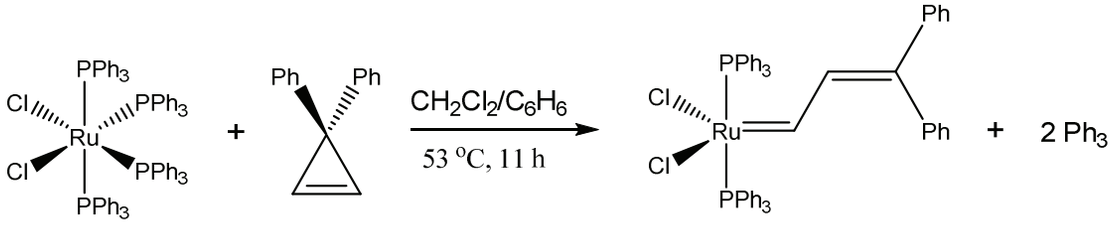
In 1976, through the example of the Fisher catalyst $WCPhR(CO)_5$ (where R═Ph or —OCH_3), described by Casey and Fisher [18, 19], Katz was the first who showed the ability of a metal-carbene complex to catalyze the process of metathesis polymerization independently without additional compounds [20]. In the history of metathesis, catalytic complexes with a well-studied structure were called "well-defined" catalysts. The discovery of "well-defined" catalysts had significantly increased the ability of ROMP to obtain polymers that have unique properties.

The first "well-defined" ruthenium catalyst was synthesized by Grubbs in 1992. The alkylidene source was 3,3-diphenylcyclopropene [21] (**Scheme 3**).

Unfortunately, this catalyst had a low activity in comparison with already available metathesis catalysts. Replacing triphenylphosphine ligands with tricyclohexylphosphine significantly improved the activity of the catalyst (**Figure 1**—1 and 2).

Later, in 1995, catalytic complexes known as first-generation Grubbs catalysts (**Figure 1**—3 and 4) were prepared using phenyl diazomethane. These catalysts not only had equal activity to molybdenum catalysts but also were indifferent to the polar groups in the monomer [22, 23].

In 1999, Grubbs reported the synthesis of second-generation catalysts (**Figure 1**—5), showing better activity and more stability at air. This catalyst was obtained by replacing tricyclohexylphosphine with an N-heterocyclic carbene ligand [24]. A year later, Hoveyda's group reported on a new type of catalytic system based on the catalysts of Grubbs of the first and second generations (**Figure 1**—6 and 7). These complexes include a chelating ester ligand [25]. Recently, a new type of ruthenium catalyst has appeared where the N-heterocyclic carbene



Scheme 3. Scheme for the Grubbs I catalyst synthesis.

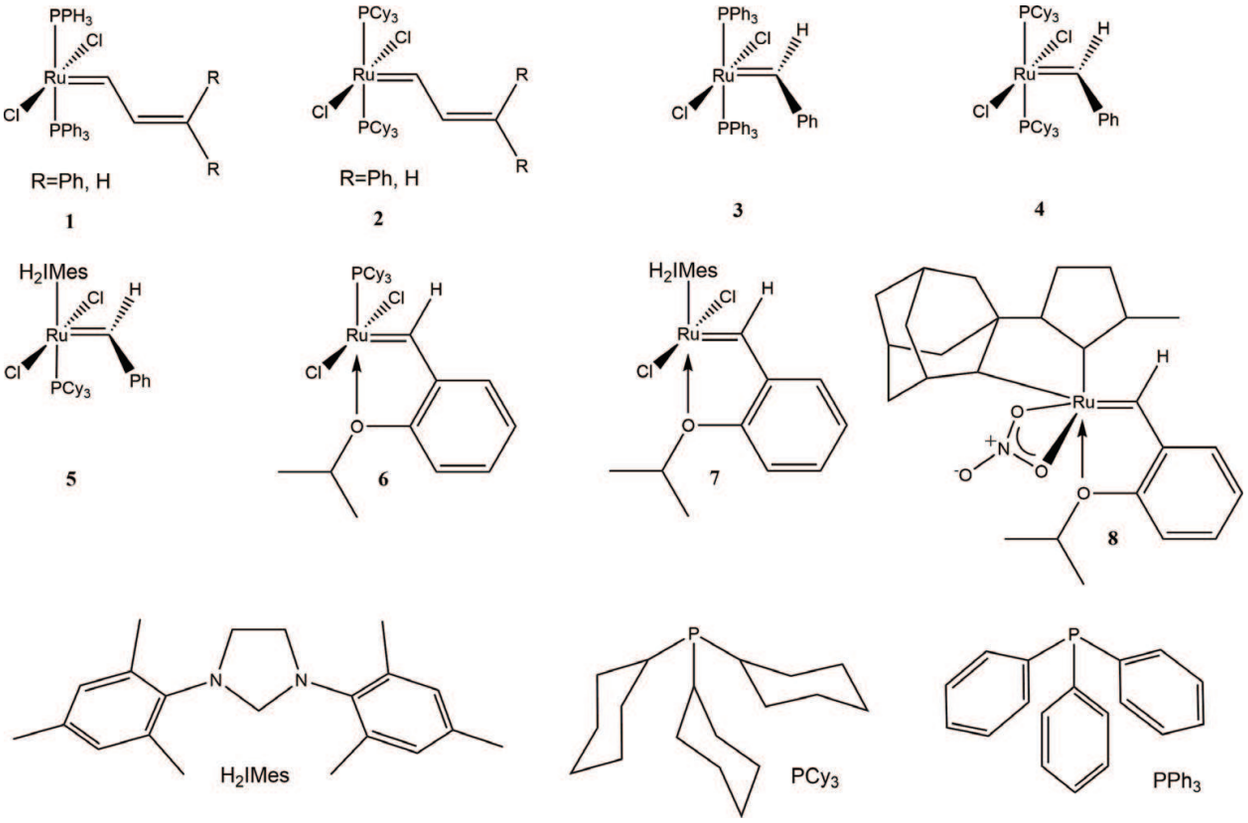


Figure 1. Main types of ruthenium catalysts.

ligand chelates the metal through the Ru-carbon bond (**Figure 1**—8). Such complexes possess high cis-selectivity in ROMP [26].

3. Reactivity of esters of 5-norbornene-2,3-dicarboxylic acid in ROMP

Currently, despite the fact that ethers of 2,3-norbornene dicarboxylic acid appear to be potential material for synthesizing polymers via ROMP, the interrelation between the molecule structure and their reactivity for metathesis polymerization with full ring opening has not been stated. A few polymerization mechanisms with different catalysts (including ruthenium) are known; however, there is no detailed description of how ethers of 5-norbornene-2,3-dicarboxylic acid behave. The study of reaction activity of 5-norbornene-2,3-dicarboxylic acid ethers with different structure using an appropriate catalyst (carbene complex of ruthenium (1,3-bis-(2,4,6-trimethylphenyl)-2-imidoazolidevynilidene)dichloro(ortho-N,N-dimethylaminomethylphenylmethylene)-ruthenium—**1** (**Figure 2**) [27] has filled this gap.

In this research, we used alkyl diesters of bicyclo[2.2.1]hept-5-en-2,3 dicarboxylic acid, obtained according to the technique given in the paper (**Figure 3**) [28].

Polymerization was carried out in NMR tubes, concurrently measuring the proton spectrum after a certain period using AU-program *zgser*.

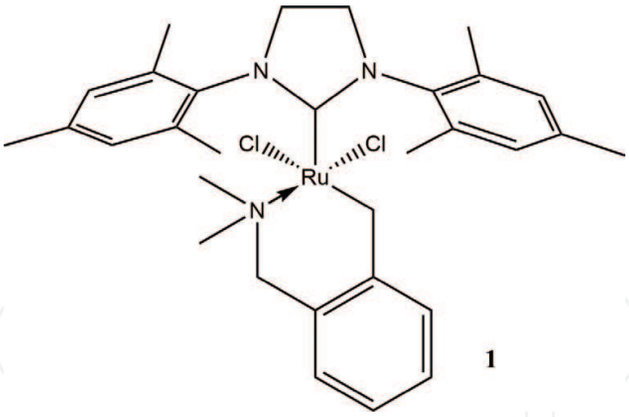


Figure 2. Catalyst complex of ruthenium used as an initiating agent for polymerization.

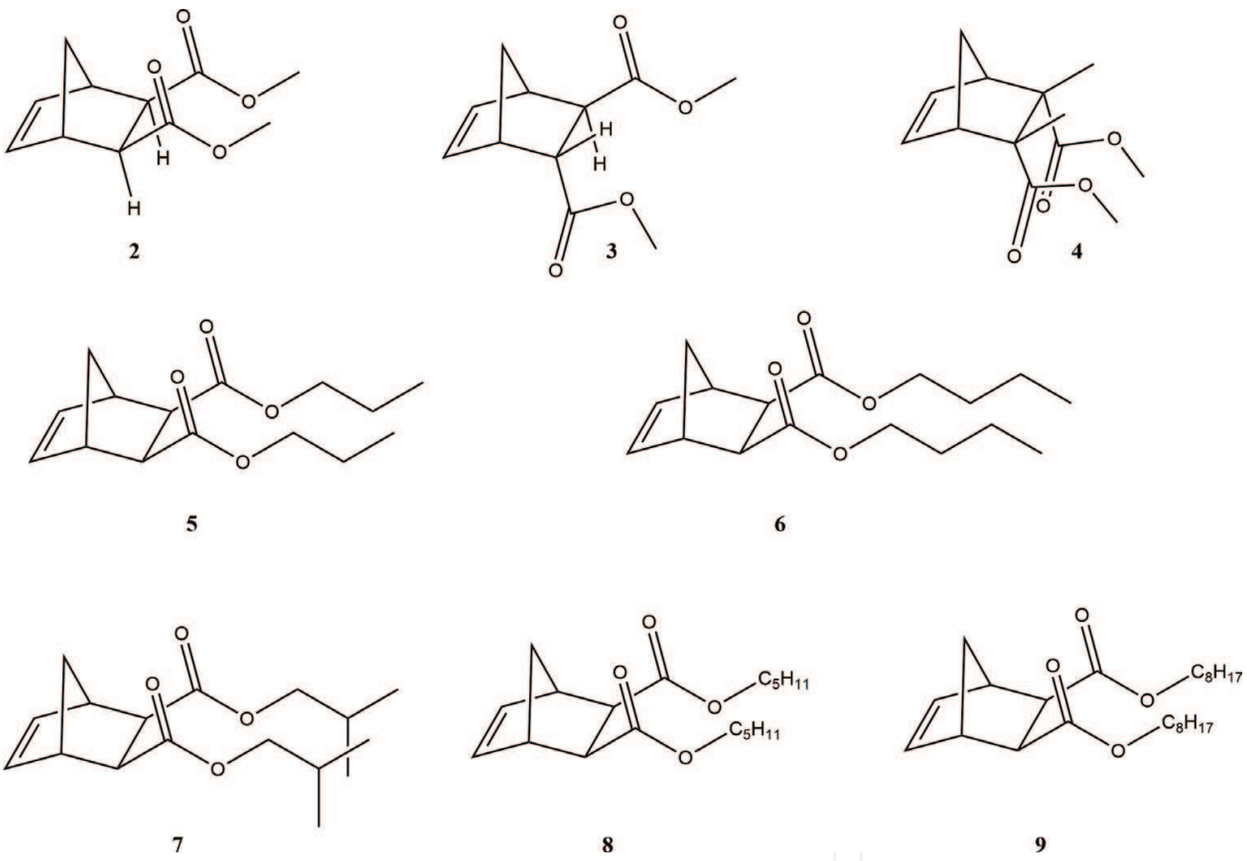


Figure 3. Alkyl diesters of bicyclo [2.2.1]hept-5-en-2,3 dicarboxylic acid, used as monomers.

The monomer concentrations were determined based on decrease and growth of integrated intensities of resonances of olefinic protons of monomer—S_M and polymer—S_P (**Figure 4**)

$$C_M = C_{M_0} \cdot \frac{S_M}{S_M + S_P} \tag{2}$$

$$C_K = C_{K_0} \cdot \frac{S_{K_0} \cdot S_S}{S_{S_0} \cdot S_K} \tag{3}$$

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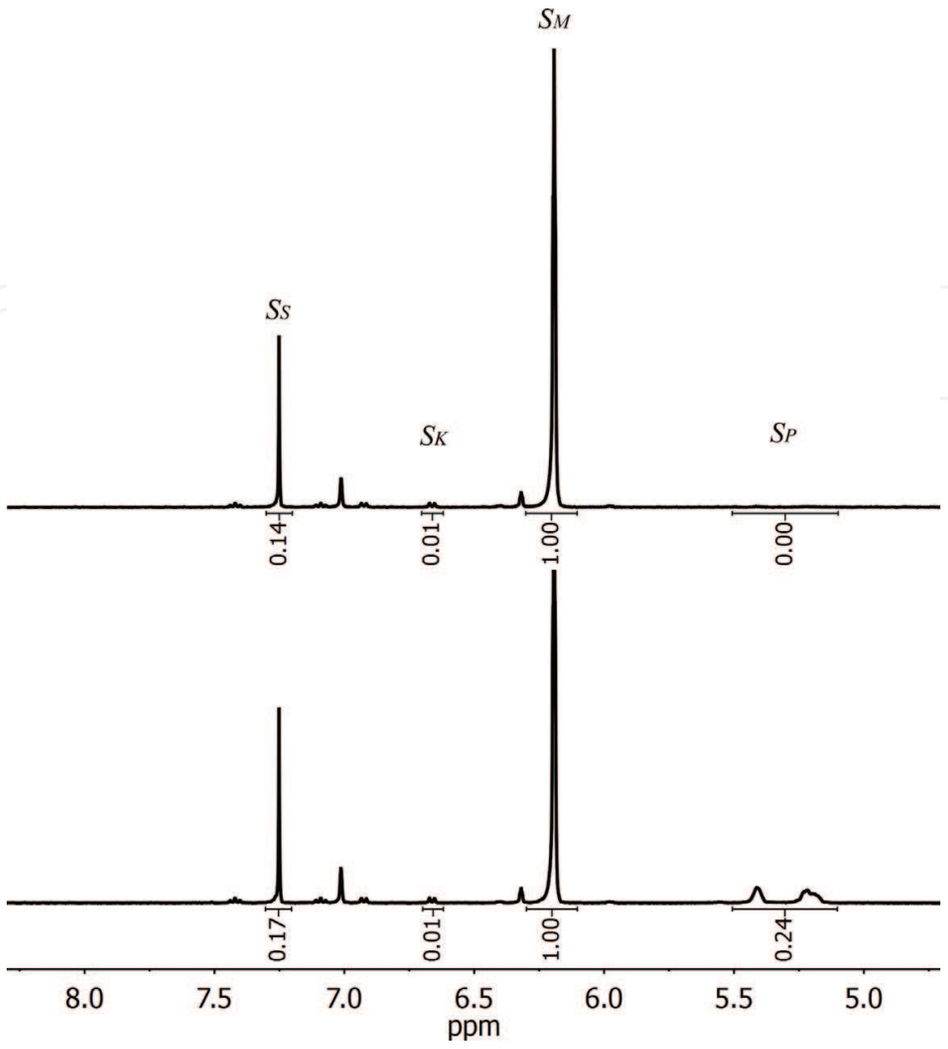


Figure 4. Combining the fragments of NMR spectra **2** in the beginning of a reaction and after 20 min.

where C_{K_0} and S_{S_0}—squares of integrated intensities of a catalyst and solvent, measured in the beginning of the reaction; S_K and S_S—current squares of integrated intensities of a catalyst and solvent during the reaction.

The AU-program *multintegr* was used to gauge the integrated intensities and time of the experiment. The using of low-viscosity solvents allowed obtaining high-resolution proton NMR spectra. Thus, kinetic studies should be carried out in the solution. And the set of monomer concentrations was defined to get kinetic correlations based on the spectral data. The solvent should be used as a diluent. **Figure 5(a)** demonstrates the curves describing the changes of concentration **2** in the course of time. According to the literature data, chloroform-d was taken as a solvent.

The molecules of chloroform-d do not react with active ruthenium and play a role of a polar medium, which stabilize 14-electron state of the active ruthenium [29]. Initially, toluene-d8 was suggested as a possible solvent, but the catalyst and monomers dissolve better in chloroform-d, which is also a widely used and more available solvent for NMR studies than toluene-d8.

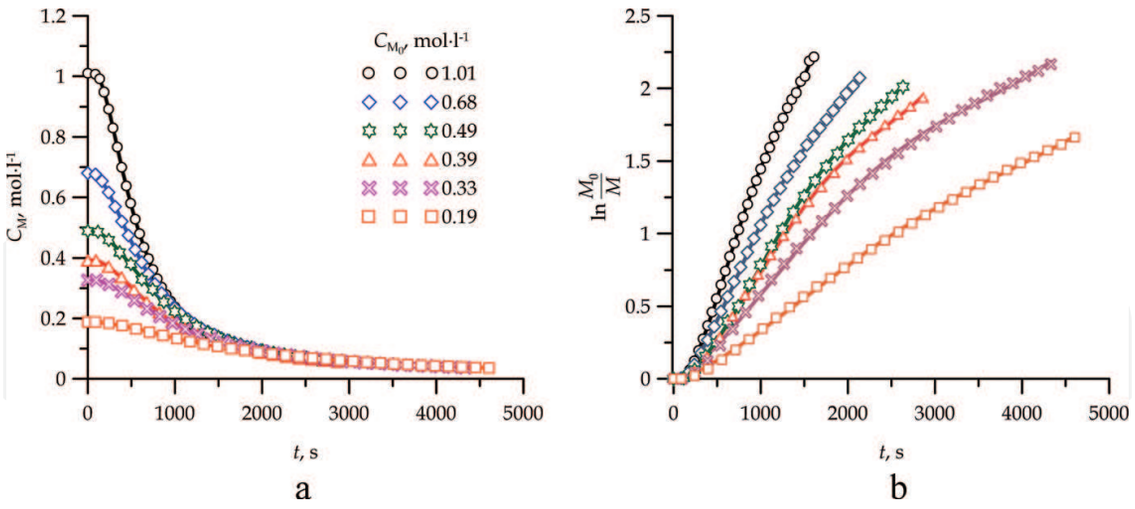


Figure 5. The decrease of monomer **2** (a) and its semi-logarithmic anamorphoses (b) during polymerization with catalyst 1 with varying initial concentration of the monomer (C_{K_0} = 0.0087 mole l^{-1}, 50°C).

Also, it was shown that reactivity of dimethyl ether of exo,exo-norbornene dicarboxylic acid is higher in chloroform-d [30]. Since chloroform-d boils at 60.9°C in ambient conditions, the operational temperature range was limited to 50°C to prevent any changes in the reactant concentration which could be caused by evaporation.

Studies [31, 32] considered the ring opening metathesis polymerization as pseudo first-order reaction as regards to the monomer concentration, which is valid for polymerization of above-mentioned monomers.

Figure 5(b) demonstrates that there can be seen three regions in the semi-logarithmic anamorphoses. The first region has non-linear segment of curve corresponding to the initiation stage. The second one is the straight-line segment prolongs to the extent of 70% monomer conversion (till one on the logarithmic scale, **Figure 5(b)**). The third region is a noticeable non-linear segment of curves, which is observed after 70% conversion. The appearance of such non-linear segments is due to the viscosity of the reaction mixture increasing, owing to the polymer molecular weight growth. This results to the fact that the polymerization rate is limited by the diffusion of monomer molecules to the active ruthenium.

Figure 6 shows the straight-line ranges of semi-logarithmic anamorphoses of polymerization **2**, catalyzed by **1**. The slope of the right lines corresponds to the observed constant of polymerization k_o.

Based on correlation coefficients given in **Table 1**, we can conclude that semi-logarithmic anamorphoses are linear in the noticed interval. **Figure 6** shows the correlation of the constant k_o and initial monomer concentration.

Figure 7 shows that k_o linearly depends on the monomer concentration within the following range from 0.2 to 1.0 mole l^{-1}, which allows to vary the monomer concentration in this range to implement kinetic experiments.

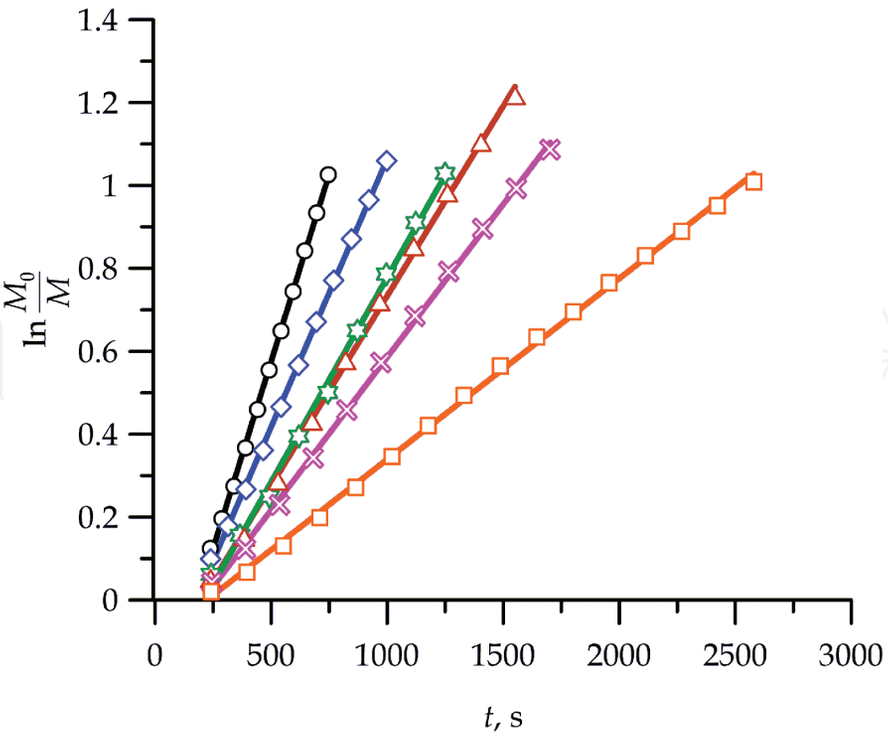


Figure 6. Linear segments of semi-logarithmic anamorphoses of monomer **2** polymerization over catalyst **1** (C_{K_0} = 0.0087 mole l^{-1}, 50°C, dependences are marked in accordance with **Figure 5**).

C_{M_0}, mole l^{-1}	*a*	*b*	*r*	$10^3 \cdot k_o$
1.01	0.00183	−0.3417	0.999	1.83
0.69	0.00131	−0.2416	0.999	1.31
0.49	0.00094	−0.1992	0.999	0.94
0.39	0.00089	−0.1614	0.999	0.89
0.33	0.00070	−0.1116	0.998	0.70
0.19	0.00042	−0.0751	0.999	0.42

Table 1. Values of k_o which calculated out of linear dependences on **Figure 6**.

Ruthenium complex should be activated to initiate polymerization. This is carried out by the first addition of monomer, which is initiation stage as well. There exist several possible mechanisms of activation; however, based on the literature data, it is assumed that bulky olefins, including the research monomers, interact with active ruthenium on a dissociative mechanism [33]

$$K \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} K^* \xrightarrow{+M\ k_2} P^*$$

The initiation rate equals the rate of active centers formation P^*. The active centers formation occurs in two stages. As it can be seen from **Figure 8**, the concentration of ruthenium complex slightly changes.

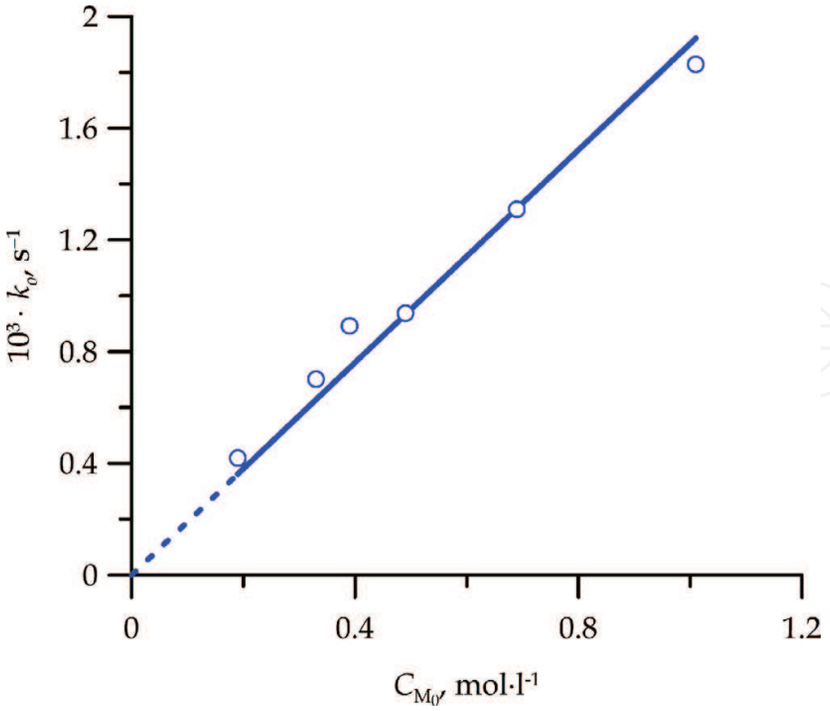


Figure 7. Correlation of the observed constant k_o of monomer **2** polymerization, catalyzed by **1** with the initial monomer concentration (C_{K_0} = 0.0087 mole l^{-1}, 50°C).

Its decrease is 1–2% from the initial catalyst concentration. Synthesized polymers at these conditions possess high molecular weight (**Table 2**).

Based on **Figure 8** and **Table 2**, we can conclude that the formation of active centers is slower than the growth of polymer chain. The research [34] also confirmed this, stating that for polymerization of exo-exo-5,6-bi(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-2-ene over Grubbs catalyst of the first generation the correlation of constants is k_i/k_g = 0.23. Moreover, the study [29] suggests that the correlation k_i/k_g is even lesser and equals 0.03 for catalyst with N-chelating ligand. In addition, based on the data presented, we can assume that disassociating of nitrogen defined by constant k_1 is limiting in the initiation reaction. Notably that the monomer molecule does not interact during initiation, that is why the formation rate of the active ruthenium complex K^* only depends on the temperature and initial concentration of ruthenium complex. Thus, the structure of the monomer molecule can affect the second stage of initiation defined by constant k_2 and the stage of polymer chain growth defined by constant k_g (it is suggested that constants of different stages of polymerization are equal $k_g^1 = k_g^2 = \ldots = k_g$)

$$P^* + M \xrightarrow{k_g^1} P^*M$$
$$P^*M + M \xrightarrow{k_g^2} P^*M_2$$
$$\ldots$$
$$P^*M_n + M \xrightarrow{k_g} P^*M_{n+1}$$

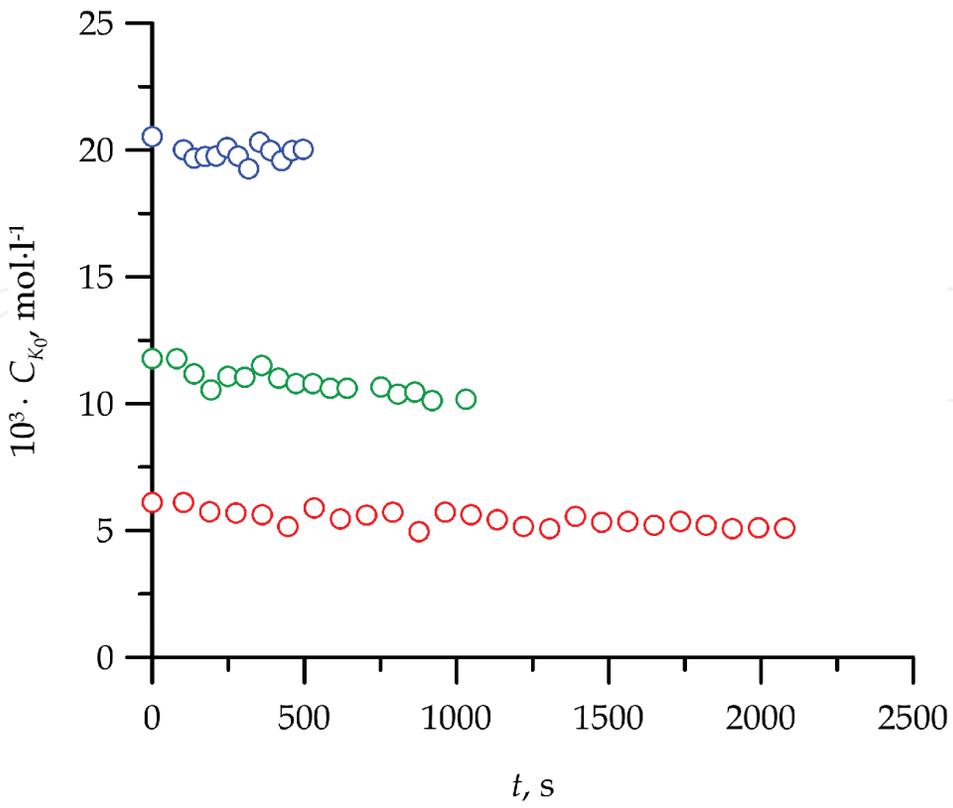


Figure 8. Ruthenium complex decrease during polymerization of monomer **2** with different initial concentration of catalyst **1** (C_{M_0} = 0.35 mole l^{-1}, 50°C).

C_{K_0}, mole l^{-1}	C_{M_0}/C_{K_0}	$10^{-5} \cdot M_n$, g mole^{-1}
0.021	17	8.5
0.012	30	10.1
0.006	57	7.6

Table 2. Average molecular weight of the obtained polymers depending on the number of initial reagents.

Kinetics of monomer consumption is complicated (**Figures 5(a)** and **9**).

In polymerization, a monomer is used during initiation and growth of the polymer chain

$$-\frac{dC_M}{dt} = k_2 \cdot C_{K^*} \cdot C_M + k_g \cdot C_{P^*} \cdot C_M \quad (4)$$

The concentration of active ruthenium complex C_{K^*} and concentration of active chains C_{P^*} are low, with C_{P^*} due to the absence of reactions of termination [5, 6] and transfer [22] of the chain constantly increases during the reaction. Since k_1 is much lesser than constants k_{-1} and k_2, it is possible to apply the principle of quasistationary for concentration of the active form C_{K^*}:

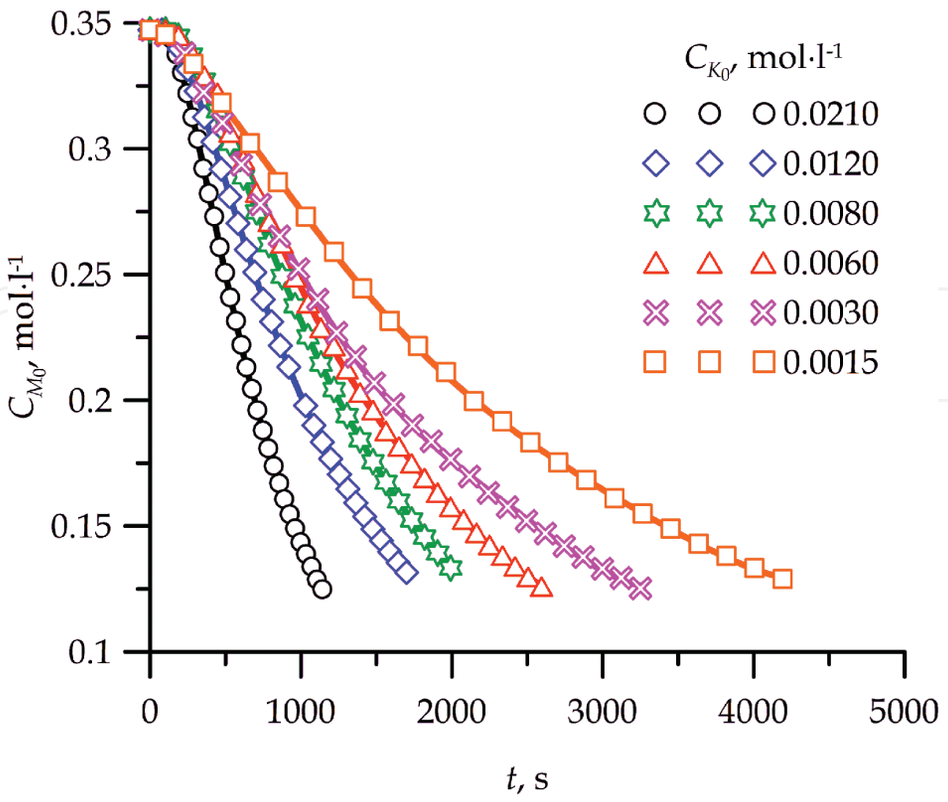


Figure 9. Monomer **2** consumption in the polymerization reaction over varying initial catalyst concentration C_{M_0} = 0.35 mole l^{-1}, 50°C).

$$\frac{dC_{K^*}}{dt} = k_1 \cdot C_K - k_{-1} \cdot C_{K^*} - k_2 \cdot C_{K^*} \cdot C_M = 0 \tag{5}$$

$$C_{K^*} = \frac{k_1 \cdot C_K}{k_{-1} - k_2 \cdot C_M} \tag{6}$$

The second stage of the initiation reaction can be viewed as pseudo first-order one proceeding with effective constant $k_{2_e} = k_2 \cdot C_{M_0}$. This assumption is fair as $C_{K_0} \ll C_{M_0}$ and $C_{K_0} \gg C_{K^*}$. Taking into consideration that the catalyst concentration slightly changes during the reaction, it could be considered that $C_K \cong C_{K_0}$. Then, changes in the concentration of active chains over time are defined by the following equation:

$$\frac{dC_{P^*}}{dt} = \frac{k_1 \cdot C_{K_0}}{k_{-1} - k_2 \cdot C_{M_0}} \cdot k_2 \cdot C_{M_0} \tag{7}$$

After integrating we get:

$$C_{P^*} = \frac{\frac{k_1}{k_{-1}} \cdot k_2 \cdot C_{K_0} \cdot C_{M_0}}{1 + \frac{k_2}{k_{-1}} \cdot C_{M_0}} \cdot t \tag{8}$$

The amount of active chains is equal to the decreasing of the monomer, which is forming these chains. Knowing the active chains' concentration from Eq. (8), the change in monomer concentration in time can be described by Eq. (9):

$$-\frac{dC_M}{dt} = \frac{\frac{k_1}{k_{-1}} \cdot k_2 \cdot C_{K_0} \cdot C_{M_0}}{1 + \frac{k_2}{k_{-1}} \cdot C_{M_0}} + \frac{\frac{k_1}{k_{-1}} \cdot k_2 \cdot C_{K_0} \cdot C_{M_0}}{1 + \frac{k_2}{k_{-1}} \cdot C_{M_0}} k_g \cdot C_M \cdot t \tag{9}$$

To simplify the equation and implement semi-logarithmic coordinates for defining the rate constant, we can ignore the first component of the right side of the equation, since it contributes less if compared with the second component. This assumption is fair for the later stages of polymerization. The formula $\frac{\frac{k_1}{k_{-1}} \cdot k_2 \cdot C_{K_0} \cdot C_{M_0}}{1 + \frac{k_2}{k_{-1}} \cdot C_{M_0}} \cdot t$ can be expressed as the following product $C_{K_0} \cdot f$, where f is the effectiveness of initiation equal to $\frac{C_{P^*}}{C_{K_0}} = \frac{\frac{k_1}{k_{-1}} \cdot k_2 \cdot C_{M_0} \cdot t}{1 + \frac{k_2}{k_{-1}} \cdot C_{M_0}}$. Then, we can put it down the following way:

$$-\frac{dC_M}{C_M} = k_g \cdot C_{K_0} \cdot f \cdot dt \tag{10}$$

After integrating, we would acquire:

$$\ln \frac{C_{M_0}}{C_M} = k_g \cdot C_{K_0} \cdot f \cdot t \tag{11}$$

Taking into consideration that f for each monomer differs only by the value of k_2 constant, which depends on the structure of monomer, it is possible to compare reaction capacity and values of activation parameters using product $f \cdot k_g$.

The chain growth rate constant of polymer k_g times the effectiveness of initiation f corresponds the tangent of the slope in the straight-line segment of semi-logarithmic correlation, which equals the product of the observed constant k_o times the initial catalyst concentration C_{K_0} (**Figure 10**).

Correlations in **Figures 7** and **11** demonstrate that the observed constant of polymerization k_o linearly depends on both the initial concentration of monomer and the initial catalyst concentration.

Linear correlation of k_o from C_{K_0} is observed because Eq. (1) takes the initial concentration of catalyst into consideration. In turn, k_o linearly depends on C_{M_0} since Eq. (11) includes parameter f, which depends on the initial concentration of monomer. Based on the data presented, we can conclude that it is possible to use the effective constant $k_e = \frac{k_o}{C_{K_0} \cdot C_{M_0}}$ to compare reaction capacity of the ethers under study. The dimensionality of constant k_e correspond the dimensionality of second-order constant since the concentration of monomer is included in numerator

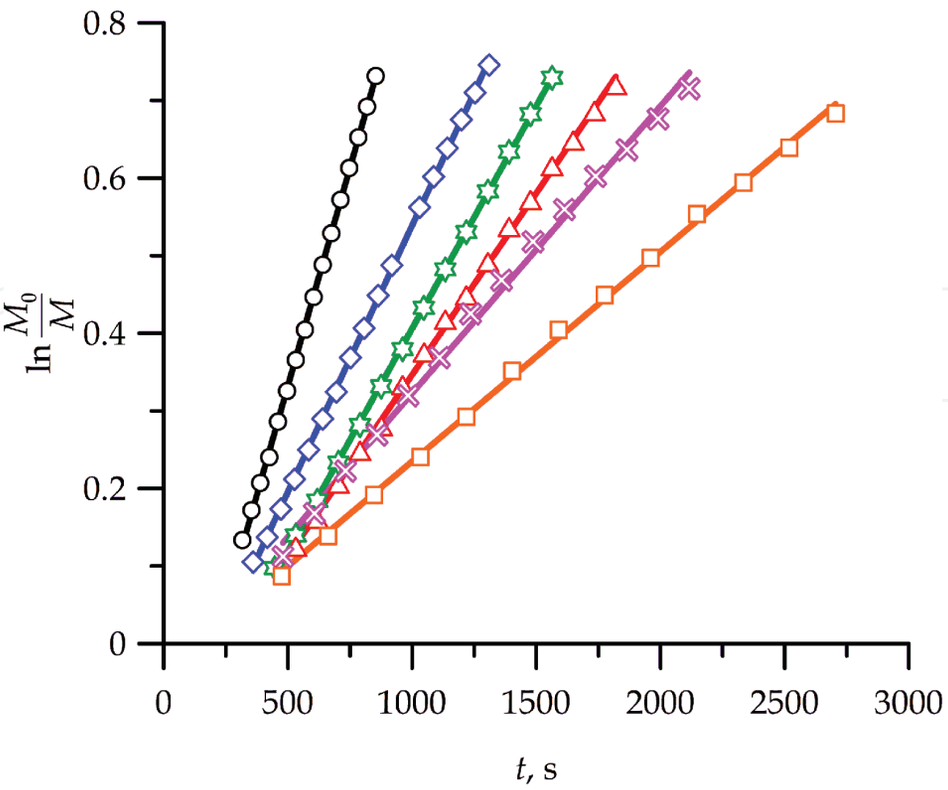


Figure 10. Semi-logarithmic correlations of polymerization **2** over catalyst **1** with varying catalyst concentration (C_{M_0} = 0.35 mole·l^{-1}, 50°C, dependences are marked in accordance with **Figure 9**).

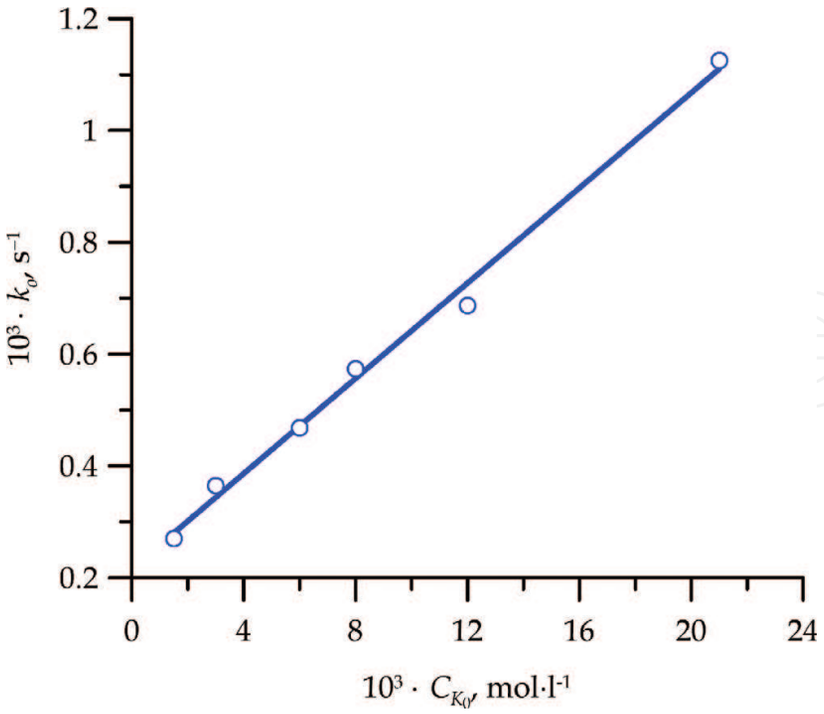


Figure 11. Correlation of the observed constant k_o of polymerization of monomer **2,** catalyzed by **1** with the initial concentration of catalyst (C_{M_0} = 0.35 mole l^{-1}, 50°C).

and denominator of the equation of the initiation effectiveness. Since constant k_o depends on the initial concentration of catalyst linearly, we can use the noticed range of concentration to estimate reactivity of esters.

4. Reactivity-structure relationship of esters of 2,3-norbornene dicarboxylic acid

Based on the values of effective constants, we compared reactivity and activation parameters of polymerization of diesters exo,exo-2,3-norbornene dicarboxylic acid, which are differ by length and branched chain of ester substituent. To define the activation parameters, we used Arrhenius equation (12) and calculation results are shown in **Figure 12**

$$\ln k_e = \ln A - \frac{E_a}{R \cdot T} \tag{12}$$

This correlation between ln k_e and $1/T$ for each researched ester has linear character. This proves that the interaction mechanism of ruthenium complex and corresponding ester at the different temperatures is unchanged. **Table 3** presents data on effective constants and activation parameters of polymerization of diesters exo,exo-2,3-norbornene dicarboxylic acid.

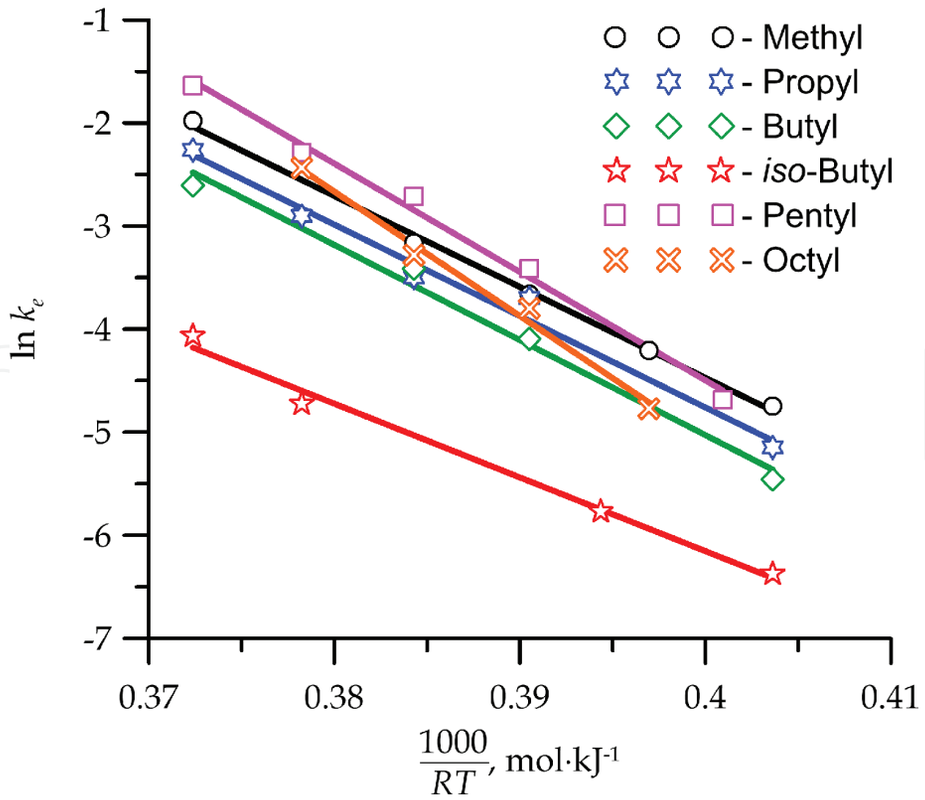


Figure 12. Arrhenius correlations of polymerization of diesters exo,exo-5-norbornene-2,3-dicarboxylic acid.

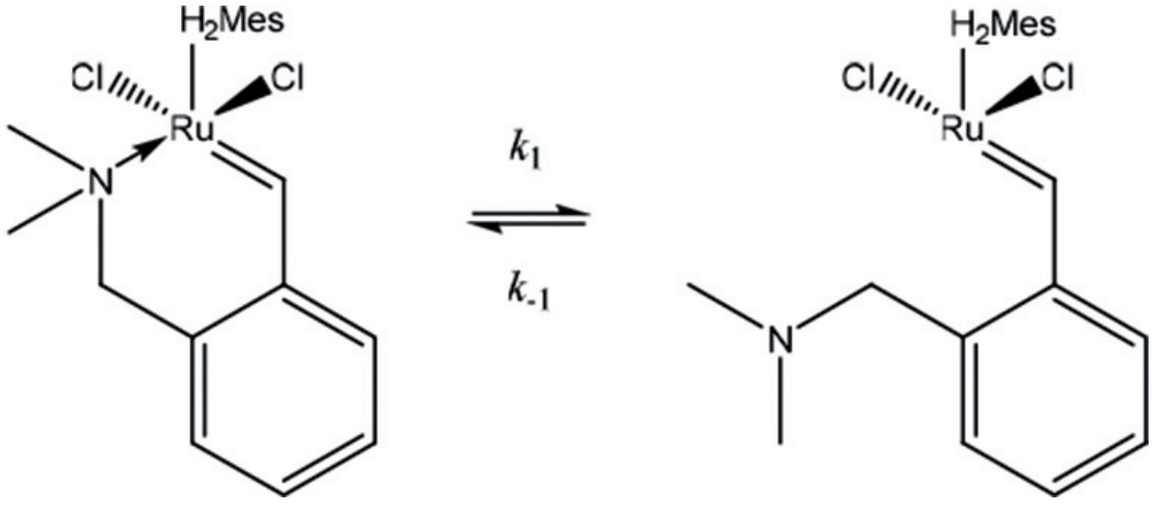
Substituent	k_e, l mole^{-1} s^{-1} (30°C)	E_a, kJ mole^{-1}	A, l mole^{-1} s^{-1}
Methyl	0.11	82	2×10^{12}
Propyl	0.10	89	2×10^{13}
Butyl	0.08	92	7×10^{13}
Iso-butyl	0.01	72	6×10^{9}
Pentyl	0.21	105	2×10^{16}
Octyl	0.17	121	2×10^{18}

Table 3. Effective constants and activation parameters of polymerization of diesters exo,exo-2,3-norbornene dicarboxylic acid.

It was expected that aliphatic radical elongation from the first to the eighth atoms of carbon would lead to gradual decrease in reactivity of esters row. However, according to **Table 5**, aliphatic radical elongation insignificantly affects the reactivity of esters.

On the contrary, branched substituent chain affects reactivity greatly. Constant k_e of an ester with iso-butyl radical is six times lesser than constant k_e of a similar ester with linear butyl radical. The steric hindrances significantly decrease the reactivity of diesters with branching aliphatic radical under interaction with active form of ruthenium complex. In study [35], the researchers attempted to make a quantitative estimation of the initiation and growth constants.

As shown in **Table 5**, the increase of aliphatic radical length leads to gradual increase of activation parameters. To explain changes in activation parameters, we should define the rate constant, which is dependent from monomer structure in more degree. Effective constant of polymerization includes four true constants. Constants k_1 and k_{-1} are determined by the structure of ruthenium complex and do not depend on the monomer structure. Nevertheless, the influence of the ester structure could be indirect. When bond Ru-N is disassociated, a 14-electron state is formed. This state is more polar than the initial 16-electron state (**Scheme 4**).



Scheme 4. Dissociation the Ru-N bond of catalyst.

Polar media stabilize 14-electron state and make disassociation easier. Solutions of esters, which are different in structure, may possess different dielectric permittivity and, thus, could affect constant k_1 and k_{-1}. However, in polymerization, solutions of esters have low concentration and the contribution of ester into the polarity of medium remains insignificant.

Esters structure would affect more constants k_2 and k_g. First, we should understand the way monomer structure can affect constant k_2. This constant defines the reaction rate, which identifies the process of monomer addition to the active form of ruthenium complex. In this process, the double bond of ester molecule occupies the vacant position in the coordination sphere of ruthenium complex (**Scheme 5**).

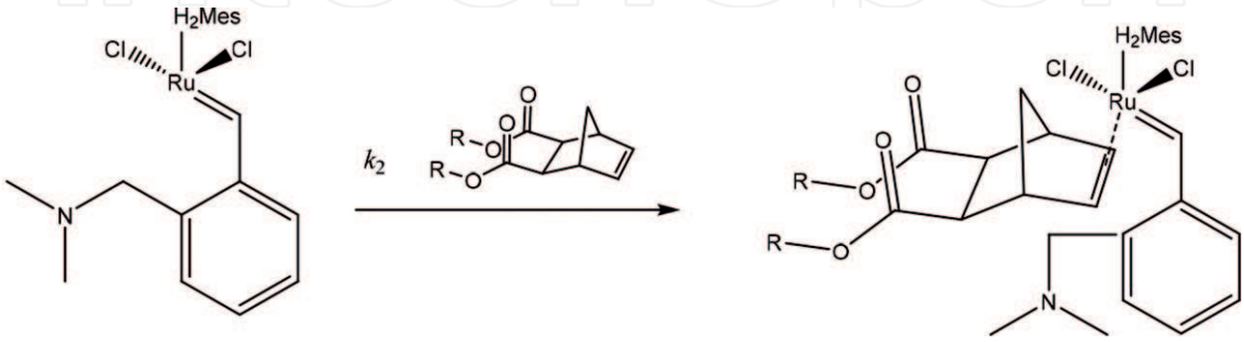
While the activation energy E_a defines excess of energy, which molecules in the reaction should possess to form transition state. Pre-exponential factor A can correlate with steric factor. Both parameters define the process of reaching the top of a potential barrier and are calculated from the initial state of the system. It is unlikely that the length of aliphatic radical affected the rate and activation parameters of this reaction. It is more probable that constant k_2 and activation parameters are nearly equal for molecules with varying length of aliphatic radical. It is also unlikely that branching substituent can affect both the rate and activation parameters of this process.

It is necessary to mention that the influence of the previous monomer unit may affect rate and activation parameters of monomer addition reaction to one of the active forms of ruthenium. However, this factor is absent on this stage of the reaction.

Having analyzed the experimental data, we concluded that the structure of monomer is more likely to affect the growth reaction of polymer chain with constant k_g.

It is known from literature data that esters of 5-norbornene-2,3-dicarboxylic acid can chelate the active forms of ruthenium complex with carbonyl oxygen of ester group, thus, forming hexatomic intramolecular complex [36]. Therefore, two active forms of ruthenium complex can take part in the polymer chain-growth reaction (**Figure 13**).

Ru—O bond strength depends on donor properties of carbonyl oxygen. In esters row, the donor properties of oxygen will enhance as there will increase inductive effect of growing radical. At the same time, Ru—O bond strength will increase. Reinforcement of Ru—O bond decreases mobility of ester fragment and makes its intramolecular complex more rigid.



Scheme 5. Coordination of the monomer's molecule with ruthenium complex.

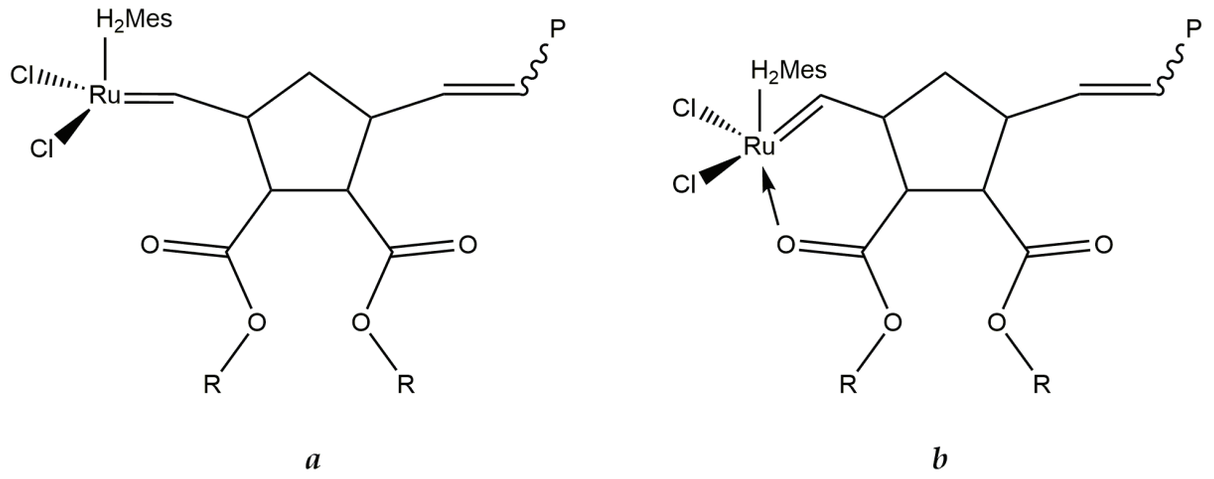
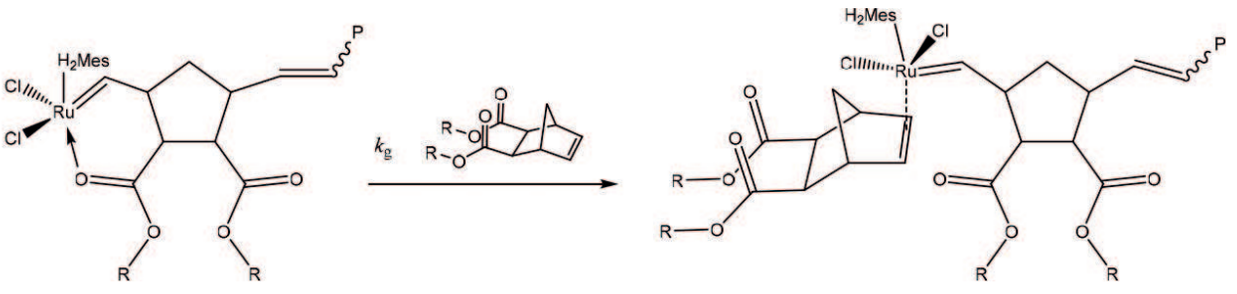


Figure 13. Non-chelated (a) and chelated (b) active forms of ruthenium complex.

When transition state is formed, monomer molecules occupy the position of oxygen in coordination sphere of ruthenium, what is accompanied by destruction of intramolecular complex (**Scheme 6**).

To degrade Ru—O bond, it is necessary to spend some energy. Lengthening of aliphatic radical, which promotes improvement of donor properties of carbonyl oxygen and intensification of Ru—O bond, increases the amount of energy needed to degrade Ru—O bond. That is why activation energy rises as the length of aliphatic radical increases. If the activation energy corresponds to the excessive energy that reacting molecules should possess to pass the potential barrier, then pre-exponential multiplier defines peculiarities of interaction of these molecules. Pre-exponential multiplier can correlate with the change of activation entropy, which depends on changes in the number of freedom degrees of the reacting molecules. Ruthenium and the previous monomer unit can form a ring with lesser number of freedom degrees than the complex they form of non-ring structure. Besides the rigidness of intramolecular complex depends on Ru—O bond strength (the more strength Ru—O bond, the more stable is intramolecular complex). Therefore, the increase of pre-exponential multiplier defined by the growth of aliphatic radical is explained by the increase in the number of freedom degrees, which appear when intramolecular complex degrades during the formation of transition state.

To form Ru—O bond, carbonyl oxygen and ruthenium should be positioned in a certain way. When Ru—O if formed, the molecule geometry is changed. Steric factor is one of the



Scheme 6. The destruction of the intramolecular complex with the addition of a new monomer's molecule.

hindrances making the formation of intramolecular complex harder. In the case of ester with branched substituent, bulky iso-butyl radicals cannot set near each other properly for carbonyl oxygen to form strength bond with ruthenium due to steric hindrances. This reduces the activation energy and pre-exponential multiplier. In addition, iso-butyl fragments of the previous monomer unit hinder the monomer placement in the coordination sphere of ruthenium, which cuts reactivity of this ester.

Figure 14 demonstrates Arrhenius correlations of constant k_e in three 3-dimensional isomers of dimethyl ester of 5-norbornene-2,3-dicarboxyl acid. The correlations are linear in the range of temperatures, which proves that the interaction mechanism of ruthenium complex and the corresponding ester is permanent.

Based on the correlations in **Figure 14**, we calculated effective constants and activation parameters of polymerization. The results are in **Table 4**.

Table 4 shows that the orientation of ester substituents to the norbornene ring affects both reactivity and activation parameters of polymerization.

The presence of substituent in endo-position reduces reaction capacity of ester. This corresponds with the data shown in other studies [34, 37–40], which estimated reaction capacity of endo- and exo-isomers of dicyclopentadiene and 2,3-dicarbomethoxy-5-norbornene. In the research of Delaude at al. [40] measured the initiation constants for monomers **2, 3**, and **4** over $[RuCl_2(p\text{-cymene})]_2$ complex activated with trimethylsilyldiazomethane; their values at 25°C were 0.040,

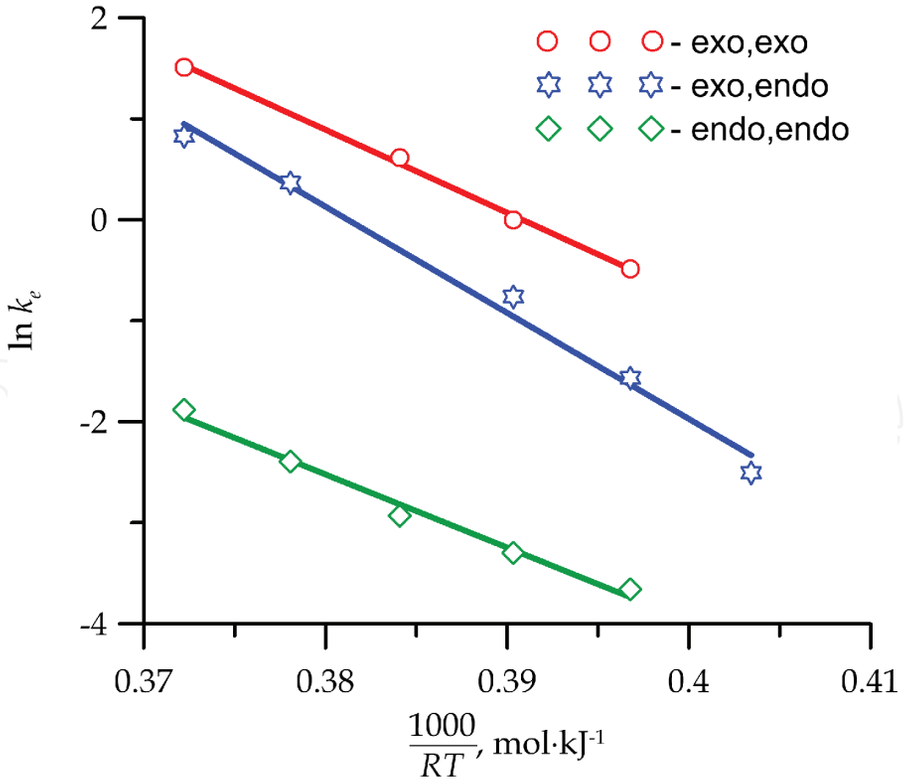


Figure 14. Arrhenius correlations of polymerization of three-dimensional isomers of dimethyl ester 5-norbornene-2,3-dicarboxylic acid.

Position	k_e, l mole^{-1} s^{-1} (30°C)	E_a, kJ mole^{-1}	A, l mole^{-1} s^{-1}
Exo,exo-	0.47	82	9×10^{13}
Exo,endo-	0.20	105	2×10^{17}
Endo,endo-	0.02	72	7×10^{10}

Table 4. Effective constants and activation parameters of polymerization of three-dimensional isomers of dimethyl ester 2,3-norbornene dicarboxylic acid.

0.025, and 0.05 l mole^{-1} s^{-1} for **2**, **3**, and **4**, respectively. At the same time, the constant of chain growth remains the same for all monomers and is within the range of 0.003–0.006 l mole^{-1} s^{-1}. The initiation stage of monomer **2** catalyzed by **1** is much slower than the chain growth stage. If we compare the constant of initiation and growth of monomer **2** catalyzed by **1** and [$RuCl_2$(p-cymene)]$_2$, then we would notice that initiation catalyzed by **1** is slower than chain growth in distinction from [$RuCl_2$(p-cymene)]$_2$, which affects initiation in a way that it is 10-fold faster than the growth of polymer chain. Comparison of constants defining polymerization initiated by these complexes is not adequate since these complexes have different structure and may have different activation mechanisms. However, in both the cases, ester groups in endo-position are located not far enough from the double bond of norbornene ring and sterically hinder the monomer attack by double bond of ruthenium. This would affect the polymerization rate of these esters both in the case of initiation by complex **1** and in the case of initiation by [$RuCl_2$(p-cymene)]$_2$. In the first case, the steric factor would affect both constants k_2 and k_g.

Each monomer is determined by its own set of activation parameters different from others. To explain the way the activation parameters change, we compiled a set of monomers in ascending order to form Ru—O bond and intramolecular complex. Exo,endo-isomer is more prone to form Ru—O bond since its ester substituents are located on different sides in relation to the norbornene ring and do not hinder each other during the formation of intramolecular complex. Ru—O bond is more strength, and intramolecular complex is more rigid in comparison with other isomers. That is why high activation energy and pre-exponential multiplier are typical for exo,endo-isomer. Exo,exo-isomer is the second on the capability to form Ru—O bond. This ester is inferior to exo,endo-isomer, since its ester substituents are located on one side in relation to norbornene ring. This sterically hinders their mutual distribution necessary for the formation of Ru—O bond. Ru—O bond has less strength, and intramolecular complex is more flexible. That is why if compared with exo,endo-isomer, exo,exo-isomer is defined by lower activation energy and pre-exponential multiplier.

Endo,endo-isomer is the third on the ability to form Ru—O bond. Because of the way ester substituents are located inside norbornene ring, this ester cannot form strong Ru—O bond. Ester group in endo-position cannot properly distribute in the coordination sphere of ruthenium to form intramolecular complex. That is why this molecule possesses low activation energy and pre-exponential multiplier.

In the paper [41], the authors estimated reactivity of these esters using the observed polymerization constant k_o as the criterion for comparing reaction capacity of monomers.

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5. Structure of polymers

The products of chemical reaction are no less valuable as a source of information for kinetic parameters. Their structure helps us to learn how reaction components interact with each other. Using NMR method to study the kinetics of metathesis polymerization of norbornene acid, ester is more beneficial since it allows estimating the structure of the obtained polymers immediately [25, 39, 42–44].

To analyze structure of polymers **2**, **5–8**, we used data from the study [39], which demonstrated that cis-units have resonances of olefinic protons in a stronger field in relation to trans-units (**Figure 15(a)**).

Overlap of resonances corresponding to cis- and trans-structures occurs in polymer obtained from monomer **4** (**Figure 15(c)**).

The spectrum of polymer **3** is more complex if compared with spectra of polymers **2** and **4**, since molecule **3** possesses chiral properties. To correlate the shifts, we applied the approach suggested in the following study [43]; it was used to analyze the structure of polymers obtained from chiral products of norbornene using NMR-spectra COSY.

Implementation of this approach alongside with assumption that resonances of olefinic protons in cis-fragments are shifted to a higher field in relation to trans-fragments [44] allowed referring resonances of olefin region to four possible structures (**Figures 15(b)** and **16**).

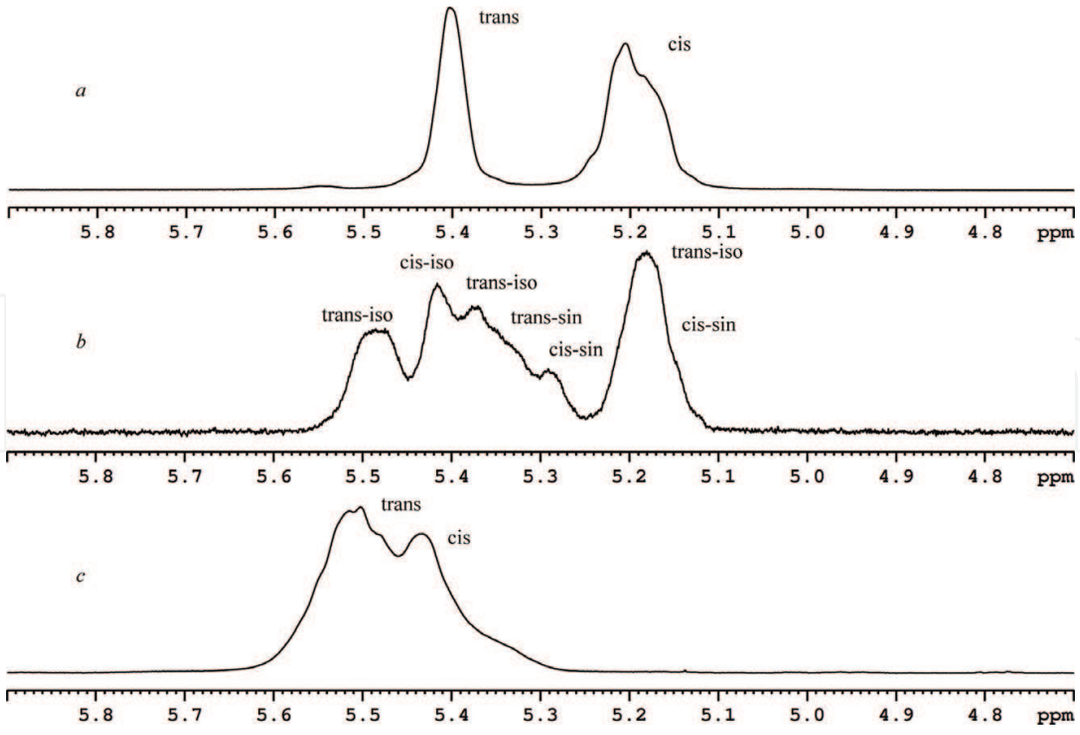


Figure 15. The region of olefinic protons ^{1}H NMR-spectra of polymers obtained with polymerization of **2–4** catalyzed by **1**.

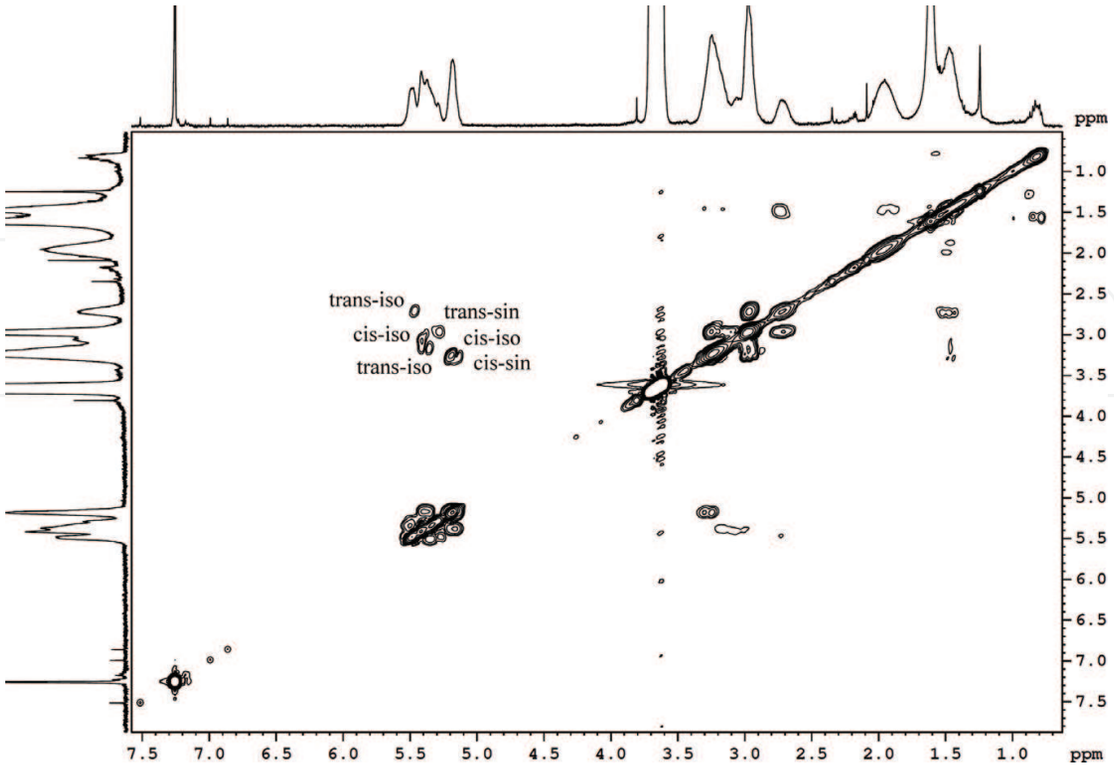


Figure 16. COSY-spectrum of polymer exo,endo-2,3-dicarbomethoxy-5-norbornene.

Monomer	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Number of cis-units in polymer, %	57	54	43	56	55	56	55
Number of trans-units in polymer, %	43	44	57	44	45	44	45

Table 5. The number of cis- and trans-units in polymers obtained during polymerization of **2–8** over **1**.

Table 5 demonstrates what of cis- and trans-units of polymers obtained from diesters of 5-norbornene-2,3-dicarboxylic acid contain.

Data given in **Table 5** only offer estimative characteristic of polymers structure but allow comparing in series monomers under study. Given these data, we can highlight that polymers obtained from exo,exo-2,3-dicarbomethoxy-5-norbornenes have a similar structure. Neither elongation of radical of ester substituent nor its branching affects the ratio of cis- and trans-fragments. The change of substituents orientation in positions 2 and 3 in relation to norbornene ring causes the change in the number of cis- and trans-structures in the case of monomer **4**. Transfer of one ester substituent from exo- into endo-position would not bring about the increase of trans-units. The situation observed can be explained if we take into consideration that there are two ways monomer molecules are attached to active ruthenium with the formation of trans- and cis-structures (**Figure 17**).

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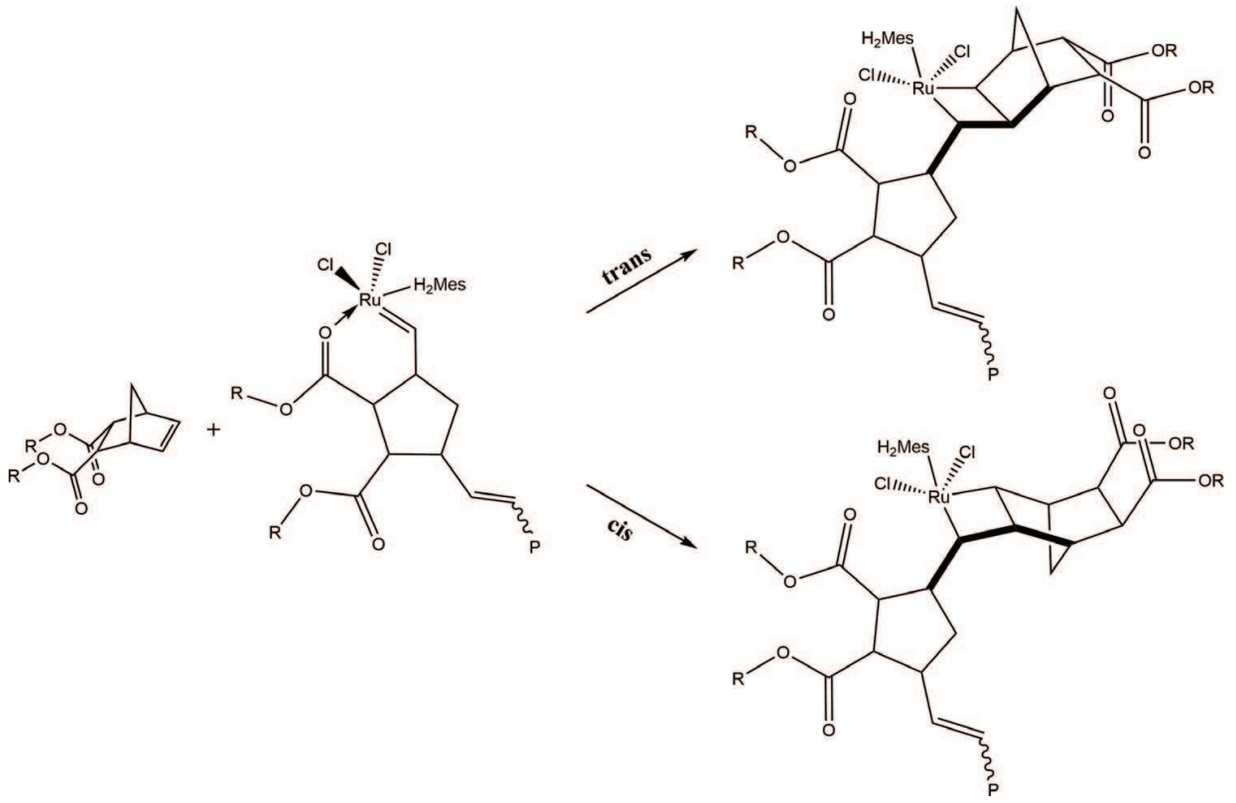


Figure 17. Two possible orientations **4** when attached to active form of ruthenium complex.

In the case when it is attached with the formation of trans-structure, a methylene bridge of norbornene ring and bulky H_2IMes-ligand hinder the monomer placement near the double bond of ruthenium. For exo,exo-derivatives, it is a more substantial hindrance if compared with ester groups which deter the attachment with the formation of cis-structures. On the contrary, for monomer **4**, two atoms of oxygen in esters are more of an obstacle for the attachment to active ruthenium than a methylene bridge of norbornene ring.

Figure 17 demonstrates that both carbonyl oxygen hinder the distribution of monomer **4** near the double bond of active ruthenium in such a way that attachment with the formation of trans-unit is sterically more beneficial. This is also seen in an increased number of trans-units in polymer obtained with monomer **4**. For monomer **3**, only one carbonyl oxygen is a hindrance and that is why the part of trans-units in the obtained polymer remains practically the same if compared with monomer **2**.

Thus, using monomers **2**, **5–8**, it is stated that the length and branching aliphatic radical of exo, exo-derivatives do not affect the ratio of cis- and trans-fragments in the obtained polymers. The orientation of ester substituents in relation to norbornene ring in 2,3-dicarbomethoxy-5-norbornenes affect the ratio of cis- and trans-fragments in polymers obtained from monomers **2–4**. The transfer of two ester substituents to endo-position increases the share of trans-units, which is due to more substantial steric hindrances caused by carbonyl oxygen of ester monomer

group and H_2IMes-ligand of catalyst when forming cis-structure if compared with the obstacles caused by methylene bridge of norbornene ring and H_2IMes-ligand of catalyst when forming trans-structure.

6. Conclusion

To summarize, it is necessary to note that metathesis polymerization with cycle opening has proved to be a powerful method of synthesizing polymers. Materials obtained with this method possess good exploitation characteristics and have already proved effective on the market of polymer goods. Development of carbene complexes based on ruthenium has made it possible to synthesize polymers from ester of 5-norbornene-2,3-dicarboxylic acid using ROMP. To obtain polymer materials by described process, a technology of injection molding in which polymerization rate matters most. Largely, polymerization rate is defined by the structure of catalyst and monomer. The activity of ruthenium catalyst complexes is well studied and apart from the structure of the complex itself it depends on a number of external factors including temperature, solvent polarity, presence of acceptor or donor compounds, etc. The structure of monomer also affects polymerization rate. It is known that steric factor during polymerization of dicyclopentadiene and oxygenated derivatives of norbornene contribute greatly to the reaction rate.

In most studies, the researchers used kinetic correlations to estimate reaction capacity of different compounds. As a rule, kinetic data are obtained with NMR method, studying polymerization *in-situ*. The technique of such experiments is well adjusted by many scholars and has proved to be effective.

Implementing this approach, it is shown how the structure of esters of 5-norbornene-2,3-dicarboxylic acid affects their reaction capacity and activation parameters in metathesis polymerization with cycle opening initiated by ruthenium complex of Hoveyda-Grubbs type II with N-chelating ligand. Taking the values of activation parameters, it is assumed that there may exist active ruthenium in chelated form, which is proved in the following studies [28, 36, 45].

It was established that the increase in the length of hydrocarbon radical does not affect greatly the reactivity, but it influences substantially the activation parameters. Branching aliphatic radical affects greatly both reactivity and activation parameters of polymerization. Based on the change in activation parameters, it might be assumed that active form of ruthenium complex forms intramolecular complex with different stability of this complex.

It was stated that mutual position of ester substituents in relation to norbornene ring affects both reactivity and activation parameters of 2,3-dicrabomethoxy-5-norbornenes. The presence of a substituent for the monomer molecule in endo-position reduces reaction capacity of this monomer [46]. Activation parameters are directly depended on the ability of monomer to form intramolecular complex with active form of ruthenium.

Based on NMR-spectra, we estimated the structures of the obtained polymers. Based on the correlation of cis- and trans-fragments, it was established that the length and branching aliphatic radical of exo,exo-2,3-dicarboxy-5-norbornenes and exo,endo-orientation of ester

substituents of 2,3-dicarbomethoxy-5-norbornene do not affect the structure of the obtained polymers. Endo,endo-orientation of two ester substituents of 2,3-dicarbomethoxy-5-norbornene increases the number of trans-units in the polymer, which is attributed to more substantial steric hindrances caused by carbonyl oxygen of monomer ester group and H_2IMes-ligand of catalyst when forming cis-structure if compared with hindrances caused by methylene bridge of norbornene ring and H_2IMes-ligand of catalyst when forming trans-structure.

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