

The Relative Reactivity of 2,3-Dicarbomethoxy-5-norbornenes in Metathesis Polymerization Using the Original N-chelating Ruthenium Carbene Complex

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ABSTRACT: ¹H NMR spectroscopy is used to study the kinetics of metathesis copolymerization of three isomeric 2,3-dicarbomethoxy-5-norbornenes using the original N-chelating ruthenium carbene complex. Based on the experimental data the copolymerization constants of isomeric 2,3-dicarbomethoxy-5-norbornenes are calculated. It is shown that the relative reactivity of endic acid dimethyl ester—(1R,2S,3R,4S)-dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate is almost two times lower than the corresponding values for (1R,2R,3S,4S)-dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate, which confirms earlier findings of steric hindrance in the orientation of the monomer due to the carbene catalyst. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40130.

KEYWORDS: dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate; the rate constant; metathesis copolymerization catalyst Hoveyda-Grubbs II; copolymerization constants; ¹H NMR spectroscopy

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INTRODUCTION

Ring opening metathesis polymerization (ROMP) is becoming more widely used in the field of macromolecular chemistry for the synthesis of polymers, allowing to obtain high molecular weight compounds with specific structures and properties.^{1–3} Metathesis polymerization processes using monomers like cyclooctene, norbornene, dicyclopentadiene and obtaining copolymers based on them have already been implemented on an industrial scale.⁴ Grubbs catalyst (Figure 1) is a well known catalyst to initiate the ROMP reactions and was also used in this research.⁵

Norbornene derivatives are widely used as monomers for ROMP^{6,7} and the monomers which are available in industrial production quantities and which we have used in our testing are esters of norbornene-2,3-dicarboxylic acid. The starting materials for their synthesis are maleic anhydride, maleic acid esters and dicyclopentadiene (DCPD) which is a by-product of the steam pyrolysis in petrochemistry.^{8,9} The possibility of industrial production of polymers based on these raw materials and the subsequent need to study the kinetics of these processes are determined by both the availability and low cost of the 2,3-dicarbomethoxy-5-norbornenes and the thermally controlled activity of the carbene complex whereby this activity allows to obtain the polymer in the bulk of the monomer. There are

three isomers of 2,3-dicarbomethoxy-5-norbornene: endo,endo-2,3-dicarbomethoxy-5-norbornene (endic acid dimethyl ester or (1R,2S,3R,4S)-dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate) (II), exo-exo-2,3-dicarbomethoxy-5-norbornene ((1R,2R,3S,4S)-dimethylbicyclo [2.2.1]hept-5-ene-2,3-dicarboxylate) (III) and exo,endo-2,3-dicarbomethoxy-5-norbornene ((1R,2R,3R,4S)-dimethylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate) (IV) (Figure 2).

Isomer IV can have the form of two optical isomers and was used in racemic form. The rate of polymerization of selected esters is highly dependent on their structure. It can be expected that the rate of polymerization of endo,endo-2,3-dicarbomethoxy-5-norbornene (II) will be the lowest as a result of steric interaction with the catalyst. The study of the relative reactivity of the isomeric dicarbomethoxynorbornene is necessary not only to determine the effect of the spatial structure of the monomers on their reactivity and selection of the most active of them, but also to provide input that is required during the calculation of optimal conditions for the implementation of the polymerization of the monomers in the industry.

EXPERIMENTAL

Esters II and III were prepared by reacting the corresponding anhydrides with methanol.¹⁰

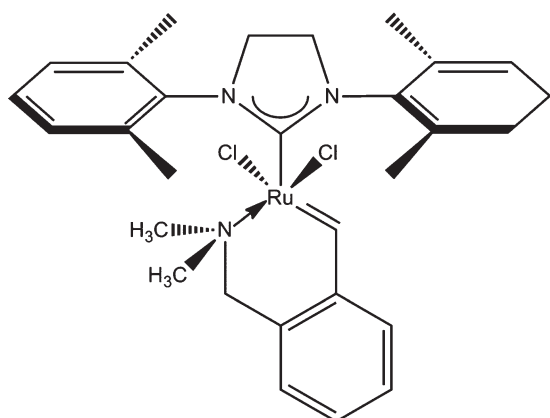


Figure 1. Structure of the catalyst which is N-chelating ruthenium carbene complex (I). One of these complexes with a thermally controlled activity was synthesized by NIOST LLC, (Russia, Tomsk).

Endo-5-norbornene-2,3-dicarboxylic anhydride from Aldrich (16.42 g, 0.10 mol), *p*-toluenesulfonic acid monohydrate (0.05 g), and 170 mL dry methanol were placed in a 250 mL round bottom flask equipped with a condenser. It was heated with stirring until it began to boil. Boiling was continued for another 6 h. Then 100 mL of methanol were evaporated from the reaction mixture and another 100 mL of dry methanol were added in reaction and boiling was continued for further 6 h. Then potassium carbonate (0.5 g) was added in reaction mixture, the excess of methanol was evaporated and endo, endo-2,3-dicarbomethoxy-5-norbornene was purified by vacuum distillation (Bp 110–112°C at 10 mBar). Ester II yield 19.3 g (91.9%) as colorless liquid.

Ester III was prepared similar to ester II procedure by using exo-5-norbornene-2,3-dicarboxylic anhydride as precursor. Ester III yield 18.7 g (89.0%) as colorless crystalline substance, Mp 51–52°C.

DCPD and dimethylfumarate were used as starting materials for the synthesis of monomer IV.¹¹

Dicyclopentadiene (95% endo isomer) was purchased from Acros Organic and used without further purification. Dicyclopentadiene (34.40 g, 0.26 mol), hydroquinone (50 mg) and dimethylfumarate (57.65 g, 0.40 mol), were placed in a 250-mL round bottom flask equipped with a condenser. Reaction mixture was heated at 160°C with stirring for 8 h. After cooling excess of dicyclopentadiene was removed at vacuum distillation.

Ester IV (Bp 115–118°C at 12 mBar) yield 71.1 g (84.6%) as colorless crystalline substance, Mp 33–34°C.

The purity of the monomers according to gas chromatography-mass spectrometry, was 97.5–99.0% (chromatograph Agilent 7890A (USA) capillary column with a diameter of 0.25 mm (5%—biphenyl, 95%—polydimethylsiloxane) and proprietary flame ionization detector, mass spectrometric detector, and autosampler for liquids)). The melting points of the monomers II, III, and IV, measured by differential scanning calorimetry, were 34.7, 51.8, and 33.5°C, respectively (instrument NETZSCH DSC 204 F1, aluminum pot, helium atmosphere, gas flow rate of 50 mL min⁻¹). ¹H NMR spectra were recorded in a solution of CDCl₃, the obtained values of the chemical shifts (δ , ppm) correspond to the literature data.

Ruthenium complex I which is soluble in the monomer at room temperature was used as a catalyst. It is stable in storage, also when in contact with oxygen and moisture in the air and therefore does not require the use of an inert atmosphere. Copolymerization of monomers II, III, and IV under the influence of catalyst complex I was studied using ¹H NMR.

A mixture of 50 mg of monomer II, III, and IV in a predetermined ratio was placed in the vial for analysis along with 400 mL of solvent CDCl₃ and the spectrum of the resulting solution was recorded. After this, 50 mL of a 1mg catalyst complex I in 1000 mL CDCl₃ was added to the vial. Monomer concentration was 0.48 mol L⁻¹, catalyst concentration was 1.6×10^{-4} mol L⁻¹ and the molar ratio of monomer to catalyst was 3000 to 1. The NMR spectrum was recorded at 30°C at regular intervals (NMR Fourier spectrometer Bruker Avance III 400—Germany).

IR spectra have been obtained using FTIR spectrometer Varian Excalibur HE3600 (Pike Miracal Multi-reflection ATR with ZnSe-diamond—USA).

RESULTS AND DISCUSSION

In the process of metathesis polymerization of norbornene, the monomer cyclic structure is expanded and forms a linear unsaturated polymer structure whilst the number of hydrogen atoms at the unsaturated C=C bonds remain unchanged. The chemical shifts of the signals of hydrogen at the double bond in the starting materials are 5.9–6.3 ppm, whereas in the resulting polymers they are shifted to 4.9–5.6 ppm, which allows the measurement of the intensities of the signals in order to track

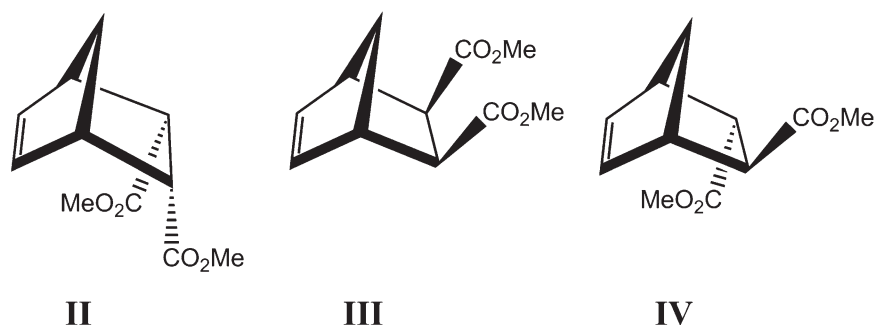


Figure 2. Structures of the isomers of 2,3-dicarbomethoxy-5-norbornene.

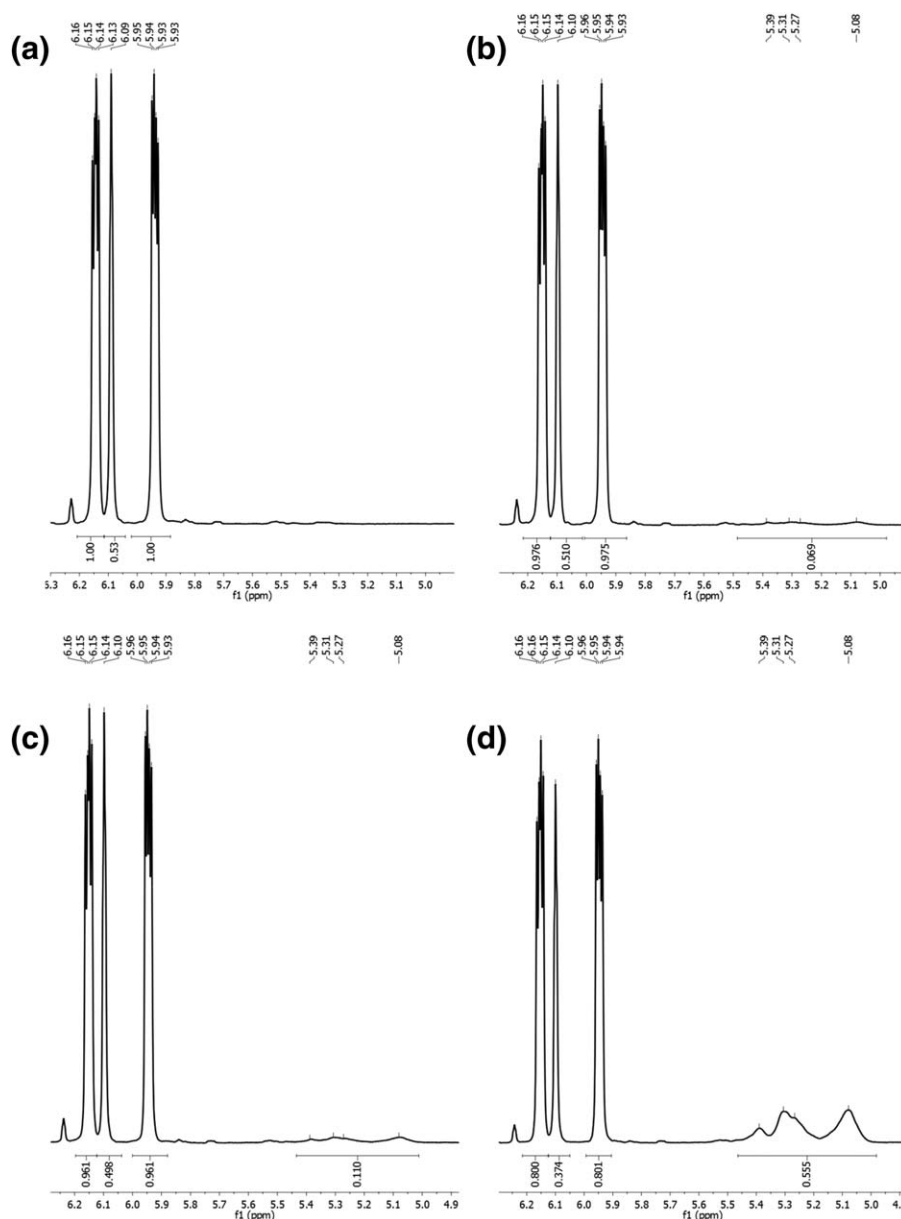


Figure 3. Fragments of ^1H NMR spectra of exo,exo- and exo,endo-isomers copolymerization (solution in CDCl_3 , ratio of monomers : catalyst = 3000 : 1, temperature 30°C , initial molar ratio of monomers – 0.2 : 0.8). Conversion: *a* – 0; *b* – 2.7; *c* – 4.4; and *d* – 22%.

the progress and explore the copolymerization related to the reactivity of the 2,3-dicarbomethoxy-5-norbornene isomer (Figure 3).

In Figure 3 peaks at 5.93, 5.94, 5.95, 5.96, 6.13, 6.14, 6.15, and 6.16 ppm belong to resonance of hydrogen at the double bond exo,endo-2,3-dicarbomethoxy-5-norbornene, peak at 6.1 ppm—resonance of

Table I. Composition of the Copolymer Calculated from the Spectra of ^1H NMR

Conversion	Integrated intensities of resonance of the double bonds			Decrease of integrated intensities of the monomers during reaction			Composition of the copolymer		
	Copolymer	Exo,endo-	Exo,exo-	Summ	Exo,endo-	Exo,exo-	Summ	Exo,endo-	Exo,exo-
0.00	0	2	0.53	2.53	0	0	0	0	0
2.73	0.069	1.951	0.51	2.53	0.049	0.02	0.069	0.710	0.290
4.35	0.11	1.922	0.498	2.53	0.078	0.032	0.11	0.709	0.291
21.94	0.555	1.601	0.374	2.53	0.399	0.156	0.555	0.719	0.281

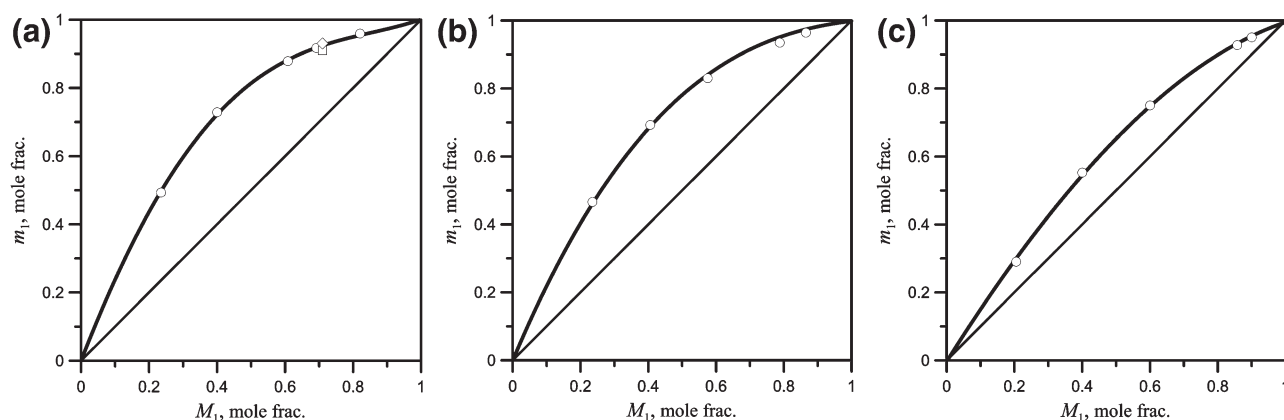


Figure 4. Graphs of the copolymer composition of exo,exo-isomer (M_1) with the endo,endo-isomer (a), endo,exo-isomer (M_1) with the endo,endo-isomer (b), exo,exo-isomer (M_1) with endo,exo-isomer (c).

Table II. Values of Isomer-Content During the Copolymerization

Exo,exo-isomer with endo,endo-isomer				Endo,exo-isomer with endo,endo-isomer				Exo,exo-isomer with endo,exo-isomer			
M_1 mole fr.		m_1 mole fr.		M_1 mole fr.		m_1 mole fr.		M_1 mole fr.		m_1 mole fr.	
Exo,exo	Endo,endo	Exo,exo	Endo,endo	Endo,exo	Endo,endo	Endo,exo	Endo,endo	Exo,exo	Endo,exo	Exo,exo	Endo,exo
1	0	1	0	1	0	1	0	1	0	1	0
0.76	0.23	0.51	0.49	0.87	0.15	0.97	0.03	0.90	0.10	0.97	0.03
0.60	0.40	0.27	0.73	0.79	0.21	0.94	0.06	0.86	0.14	0.92	0.07
0.39	0.60	0.12	0.88	0.58	0.42	0.85	0.15	0.60	0.40	0.85	0.15
0.31	0.69	0.08	0.92	0.41	0.59	0.68	0.32	0.40	0.60	0.68	0.32
0.18	0.82	0.04	0.96	0	1	0	1	0.20	0.80	0.29	0.71
0	1	0	1					0	1	0	1

hydrogen at the double bond exo,exo-2,3-dicarbomethoxy-5-norbornene, and finally peaks at 5.08, 5.27, 5.31, and 5.39—resonance of hydrogen at the double bond in the copolymer.

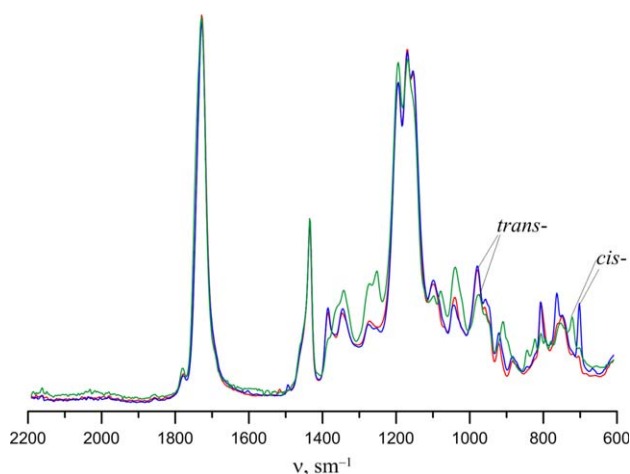


Figure 5. IR spectra of homopolymers exo,exo(-) and endo,endo-isomer (-) dicarbomethoxynorbornene copolymer and exo,exo- ($M_1 = 0.7$ mole frac.) with the endo,endo-isomer (-). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Calculation of the copolymer composition was carried out as follows. By decrease of the integrated intensity of the resonance peaks of hydrogen at the double bond of monomers was determined part thereof was incorporated in the copolymer.

Calculation of the copolymer composition was carried out by looking at the decrease of the integrated intensity of the resonance peaks of hydrogen at the double bond of monomers and at the part thereof which was incorporated in the copolymer. For the spectra in Figure 3 these values were calculated and recorded in Table I.

Results of the obtained ^1H NMR spectra of monomers are as follows.

Spectrum II: 1.31 (d 1H, $C7H\beta$, $2J = 8.6$ Hz), 1.46 (m, 1H, $C7H\alpha$, $3J = 1.84$ 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, $C5H$, $C6H$).

Spectrum III: 1.49 (m 1H, $C7H\alpha$, $3J = 1.7$ Hz, $2J = 9.3$ Hz), 2.10 (d 1H, $C7H\beta$, $2J = 9.3$ 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).

Table III. Composition of Copolymer Exo,Exo- and Endo,Endo-Isomers of 2,3-Dicarbomethoxy-5-norbornene Determined from their IR Spectrum

Polymer	Peak area in IR spectrum			Relative content of units in <i>cis</i> -configuration		Copolymer composition		
	S_{1730}	S_{1430}	S_{705}	$D_{705/1730}$	$D_{705/1430}$	M_1	m_1 on $D_{705/1730}$	m_1 on $D_{705/1430}$
Homo exo,exo-	9.62	3.03	0	0	0	0	0	0
Co exo,exo- ($M_1 = 0.7$ mole frac.) and endo,endo-	8.97	2.84	1.14 ^a	0.127	0.401	0.7	0.921	0.919
Homo endo,endo-	10.5	3.32	1.45	0.138	0.437	1	1	1

^aPeak area at ν , 720 cm^{-1} in the spectrum of the copolymer exo,exo- ($M_1 = 0.7$ mole frac.) and endo,endo-isomers of 2,3-dicarbomethoxy-5-norbornene.

Spectrum IV: 1.45 (m 1H, C7H α , 3J = 1.7 Hz, 2J = 8.8 Hz), 1.61 (d, 1H, C7H β , 2J = 8.8 Hz), 2.68 (dd, 1H, C3H, 3J = 4.5 Hz, 3J = 1.6 Hz), 3.12 (1H SS, S4N), 3.26 (1H SS, S1N), 3.37 (dd, 1H, C2H, 3J = 4.5 Hz), 3.64 (3H with, S9N3), 3.71 (a, 3H, S11N3), 6.06 (dd, 1H, S6N, 3J = 5.6 Hz, 3J = 2.8 Hz), 6.27 (dd, 1H, S5N, 3J = 5.6 Hz, 3J = 3.2 Hz).

Looking at the spectra of the monomer substituents located on the same side relative to the ring (II and III), one band can be found in the resonance of the protons of norbornene double bond. In the spectra of the monomer substituents located on either side of (IV), two bands can be found. The kinetic curve which describes the consumption of double bonds is given by the dependence of the intensity of these bands upon the reaction time.¹² These kinetic curves allow to calculate the content of isomer dicarbomethoxynorbornene in the copolymer.

The obtained values for the content of isomer 2,3-dicarbomethoxy-5-norbornene in the copolymer can be found in Figure 4 and in Table II.

Analysis of the IR spectra of homopolymers of exo,exo- and endo,endo-isomers of 2,3-dicarbomethoxy-5-norbornene (Figure 5) showed that the first one contains mainly links in the *trans*-configuration (ν , 975 cm^{-1}) and the second, along with the links of *trans*-configuration (ν , 975 cm^{-1}) also contains a significant amount of *cis*-configuration units (ν , 705 cm^{-1}). The IR spectrum of the copolymer exo,exo- ($M_1 = 0.7$ mole frac.) and endo,endo-isomer 2,3-dicarbomethoxy-5-norbornene also shows bands of *trans*- and *cis*-configuration, the latter being slightly shifted (ν , 720 cm^{-1}) relative to the position of the strip itself in the spectrum of the homopolymer endo,endo-isomer 2,3-dicarbomethoxy-5-norbornene (Figure 5). The content of the *cis*-configuration of homo- and copolymers were evaluated for relative absorption bands at ν , 705 or 720 cm^{-1} (CH bending vibrations in the *cis*-RHC=CHR') and 1730 cm^{-1} (C=O stretching vibrations in the RO-CO-CH₃) or ν , 1435 cm^{-1} (deformation vibrations of CH₂ groups) in the corresponding IR spectra (Figure 5). The resulting relative value of a content of *cis*-configuration homopolymer endo,endo-isomer 2,3-dicarbomethoxy-5-norbornene taken as 1.

The graph of the copolymer composition exo,exo-isomer (M_1) with endo,endo-isomer [Figure 4(a)] of the points marked as a

square and a diamond shape on the graph and corresponding to the content of units of exo,exo-isomer 2,3-dicarbomethoxy-5-norbornene (m_1), determined from IR spectrum copolymer (Figure 5) as described above (see Table III).

To assess the relative activity of monomers in the copolymerization we calculated copolymerization constants r_1 and r_2 for isomeric 2,3-dicarbomethoxy-5-norbornene. For their determination we used the graphical methods: Kelen and Tüdös, Fineman and Ross, and others.^{13,14} As an example of defining r_1 and r_2 , Figure 6 shows the dependence of η upon ζ (equation parameters and Kelen Tüdös) for the systems under study.

Kelen and Tüdös proposed a new linear graphical method that takes into account the degree of scatter of the experimental data by a factor α . The Kelen–Tüdös equation

$$\eta = \left(r_1 + \frac{r_2}{\alpha} \right) \zeta - \frac{r_2}{\alpha} \quad (1)$$

where $\eta = G/(\alpha + E)$; $\zeta = E/(\alpha + E)$.

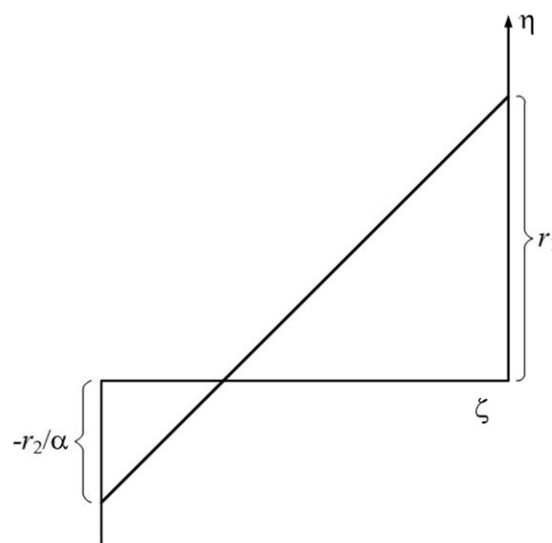


Figure 6. Graphical determination of relative reactivity ratios according to Kelen and Tüdös.

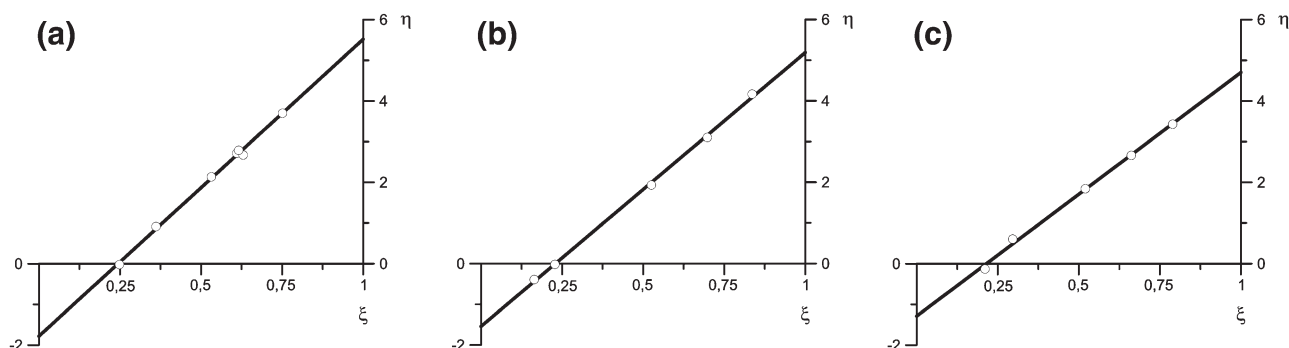


Figure 7. The dependence of the parameters of the equation and Kelen Tüdös for copolymers exo, exo and endo, endo-isomers (a) and exo, exo-and endo, endo-isomers (b), exo, endo-and endo, endo-isomers (c).

The parameter α is determined as follows:

If E_{\min} and E_{\max} have different signs, then $\alpha = -(E_{\min} + E_{\max})/2$.

If E_{\min} and E_{\max} have the same sign then $\alpha = \text{SQRT}(E_{\min} \times E_{\max})$ where E_{\min} and E_{\max} are the extreme values in the range of experimental data.

The equation gives important information about the mechanism of polymerization. Available data on copolymerization can be attributed to three classes: (a) systems in which the copolymerization mechanism is described by the conventional equation and the two-parameter model can be used, (b) systems in which complete approximation to the basic equation of the copolymer composition is impossible and (c) systems in which

Table IV. Calculated Values of Reactivity Ratios of Exo,Exo-Isomer (r_1) to Endo,Endo-Isomer (r_2)

Method of determination	Exo, exo-isomer (r_1)	Endo, endo-isomer (r_2)	Correlation coefficient
Fineman-Ross right	5.53 ± 0.09	0.51 ± 0.04	0.999
Fineman-Ross left	5.6 ± 0.1	0.55 ± 0.03	0.998
Kelen-Tüdös	5.6 ± 0.1	0.53 ± 0.04	0.998
Esrielev-Brohina-Roskin	5.6 ± 0.1	0.53 ± 0.04	0.999

Table V. Calculated Values of Reactivity Ratios of Exo,Exo-Isomer (r_1) to Endo,Exo-Isomer (r_2)

Method of determination	Exo, exo-isomer (r_1)	Endo, exo-isomer (r_2)	Correlation coefficient
Fineman-Ross right	2.3 ± 0.1	0.73 ± 0.05	0.998
Fineman-Ross left	2.18 ± 0.04	0.67 ± 0.08	0.999
Kelen-Tüdös	2.20 ± 0.08	0.70 ± 0.05	0.998
Esrielev-Brohina-Roskin	2.20 ± 0.07	0.70 ± 0.06	0.997

the use of the copolymer composition equation is totally insufficient based on the two-parameter model. For systems (b) and (c) no linear relationship is observed.

Kelen and Tüdös also proposed a variant of the method¹⁵ which allows to determine the reactivity ratios at high degrees of conversion. In this case it is necessary to amend the degree of conversion.

$$Z_1 = [M_1]/[M_1]_0 \text{ and } Z_2 = [M_2]/[M_2]_0 \text{ whereas}$$

$$E = (m_1 \cdot m_2) \cdot (\ln Z_2 / \ln Z_1)^2; G = ((m_1 / m_2) - 1) \cdot (\ln Z_2 / \ln Z_1).$$

Like this, the Kelen and Tüdös method allows the calculation of reactivity ratios during the polymerization process of up to 50% conversion.

The value r_1 is directly obtained from the slope of the eq. (1) at the point of intersection of the axis of ordinates in $\zeta = 1$ and the value r_2/α (at the intersection of the axis of ordinates in $\zeta = 0$). The values of the reactivity ratios can be readily determined either or computed using the least squares method. The relationship $\eta = f(\zeta)$ can be seen in Figure 7 and is a straight line in the range from 0 to 1 and shows that the system can be adequately described by the equation of the copolymer composition.

Figure 7 shows that the copolymerization follows the two-parameter model since the dependence of η upon ζ is linear with a correlation coefficient close to one.

Tables IV–VI show the copolymerization constants for systems of exo, exo-isomer: endo, endo-isomer, exo, exo-isomer: endo,

Table VI. Calculated Values of Reactivity of Endo,Exo-Isomer (r_1) to Endo,Endo-Isomer (r_2)

Method of determination	Endo, exo-isomer (r_1)	Endo, endo-isomer (r_2)	Correlation coefficient
Fineman-Ross right	4.2 ± 0.2	0.51 ± 0.04	0.998
Fineman-Ross left	4.4 ± 0.3	0.6 ± 0.2	0.999
Kelen-Tüdös	4.3 ± 0.2	0.51 ± 0.08	0.998
Esrielev-Brohina-Roskin	4.3 ± 0.2	0.52 ± 0.09	0.863

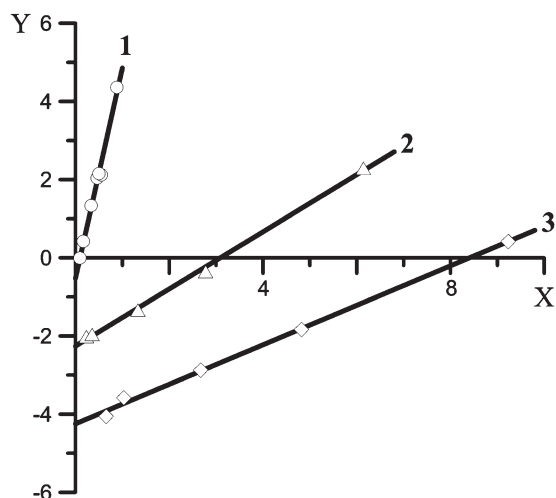


Figure 8. Dependence of $Y = (M/(1-M)) \cdot (g - (1-m)/m)$ on $X = M^2 \cdot (1-m) / m \cdot (1-M)^2$ for copolymers exo,exo and endo, endo-isomer (1), exo,exo-and exo,endo-isomer (2) and exo,endo- and endo,endo-isomer (3).

exo-isomer and exo, endo-isomer: endo, endo-isomer, calculated by different methods.¹⁶

In Tables IV and V, the found constants ($r_1 < 1$ and $r_2 > 1$) indicate that these isomers form a random copolymer and the exo,exo-isomer is the more active isomer. The product $r_1 \times r_2 > 1$ so it can be argued that the exo,exo-isomer is preferable better connected not only to itself but also to other active components.

In Table VI, the found constants ($r_1 < 1$ and $r_2 > 1$) indicate that these isomers form a random copolymer and the endo,exo-isomer is the more active isomer. The product $r_1 \times r_2 > 1$ so it can be argued that the endo,exo-isomer is preferable better connected not only to itself but also to other active components.

Further evidence of the uncomplicated character of the copolymerization of isomeric dicarbomethoxynorbornene can be found in $Y = (M / (1-M)) \cdot (g - (1-m)/m)$ on $X = M^2 \cdot (1-m) / m \cdot (1-M)^2$ shown in Figure 8 (where g —the ratio of the molecular weight of the monomers, and m and M —the copolymer composition and monomer content in the starting mixture, respectively). In Figure 8 we see that the linear relationship is well respected where these values have high correlation coefficients which are close to one.

CONCLUSIONS

Copolymerization of exo,exo-, endo,endo-, and exo,endo-isomers of 2,3-dicarbomethoxy-5-norbornene was investigated in

CDCl_3 solution using the original Hoveyda-Grubbs II catalyst. The composition of the copolymer was determined using ^1H NMR-spectroscopy as well as by the content of cis-configuration of units in the IR-spectrum of the exo,exo- and endo,endo-isomers of 2,3-dicarbomethoxy-5-norbornene. Exo,exo-isomer of 2,3-dicarbomethoxy-5-norbornene is a more active monomer than exo,endo- and endo,endo-isomers in the copolymerization.

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