

Computational study of metathesis degradation of rubber. distributions of products for the ethenolysis of 1,4-polyisoprene

Selena Gutierras, Sergio Martinez Vargas, Mikhail A. Tlenkopatchev*

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, CU, Coyoacán, Mexico DF 04510, Mexico

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Abstract

The molecular modeling of the product distributions for the ethenolysis of 1,4-polyisoprene at 25 °C using the B3LYP/6-31G(d,p) level of theory reveals that chain–ring and chain–chain equilibria are completely shifted toward the formation of 2-methyl-1,5-hexadiene. The amount of cyclic oligomers at equilibrium with linear molecules is small. The concentration of 2-methyl-1,5-hexadiene at equilibrium with linear isoprene oligomers is of 90 mol%. The value of 1,5-hexadiene at equilibrium with butadiene oligomers for the ethenolysis of 1,4-polybutadiene corresponds to 46 mol%. These results are in agreement with experimental data.

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1. Introduction

The metathesis reaction leads to the equilibrium between all species formed during the exchange of the double bonds and thermodynamic data can be used for the prediction and calculation of product distributions at equilibrium state. The experimental and theoretical investigations demonstrated that the ethenolysis and intramolecular metathesis degradation of *cis*-polybutadiene (*cis*-PB) are thermodynamically favored and chain–chain and chain–ring equilibria are shifted toward the formation of 1,5-hexadiene and the all *trans* cyclic trimer [1–5].

The metathesis degradation of polyalkenamers has been studied for over 30 years [6]. The intramolecular metathesis degradation of many polyalkenamers and its cross-metathesis with linear olefins as chain transfer agents (CTAs) to produce low molecular weight and end-functionalized oligomers have been performed using tungsten, molybdenum and ruthenium based catalysts [1–3,7–13].

Few reports exist on the metathesis degradation of *cis*-1,4-polyisoprene (*cis*-PI, natural rubber) [14–17]. This may be explain by the fact that *cis*-PI is very sensitive to the side reactions [15] and this polymer with trisubstituted unsaturations degraded much more slower than *cis*-PB [18]. The authors [18] reported that the intramolecular degradation of *cis*-PI using the classical tungsten based catalyst took more than 200 h to form cyclic oligomers. Recently, it has been shown that the use of the extremely high active ruthenium catalyst containing a N-heterocyclic carbene ligand leads to the rapid and efficient metathesis degradation of *cis*-PI [19]. Numerous experiments show that the intermolecular metathesis degradation of rubber is accompanied by intramolecular cyclization to form a set of thermodynamically stable cyclic oligomers [6] (Fig. 1).

Earlier, authors [20] demonstrated that the intermolecular metathesis of *trans*-PI with ethylene by a tungsten alkylidene catalyst produced the isoprene oligomers with trace amounts of 2-methyl-1,5-hexadiene. It means that the highly efficient long-lived metathesis catalysts will depolymerize the isoprene rubber to the expected monomeric diene 2-methyl-1,5-hexadiene.

The purpose of the present study is to examine the concentration of 2-methyl-1,5-hexadiene at equilibrium

* Corresponding author. Tel.: +52-5622-45-86; fax: +52-5616-12-01.

E-mail address: tma@servidor.unam.mx (M.A. Tlenkopatchev).

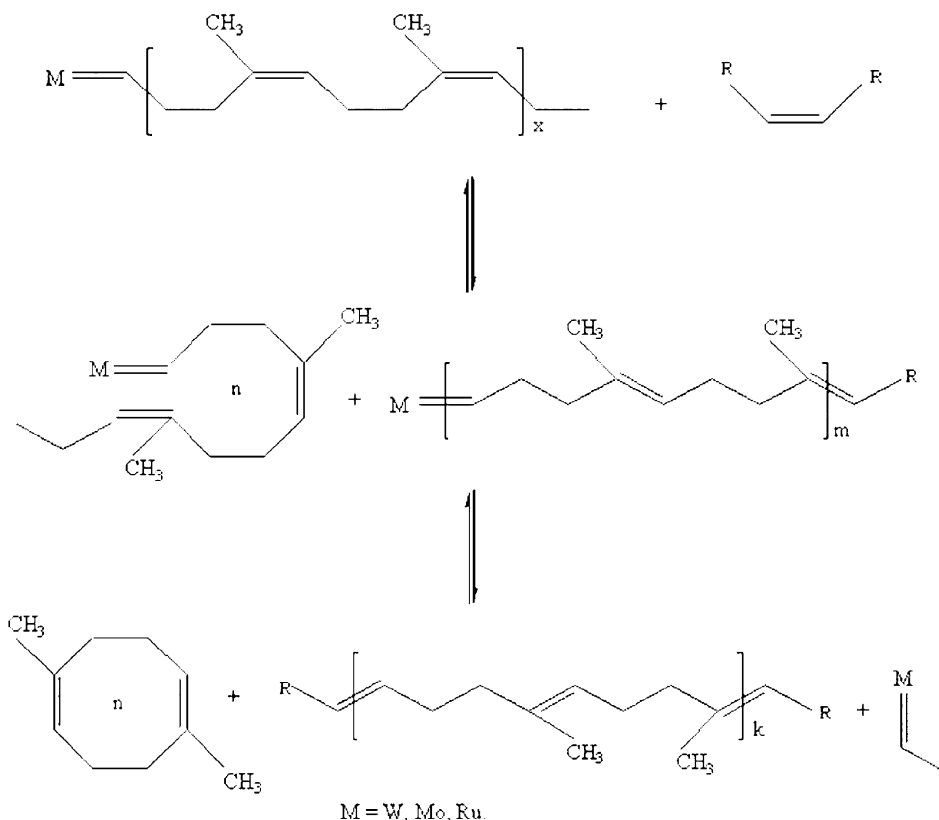


Fig. 1. Intermolecular degradation of *cis*-PI via metathesis.

with cyclic and linear oligomers for the ethenolysis of 1,4-polyisoprene (1,4-PI) using ab initio approach.

2. Computational methods

All geometry optimizations were carried out using Gaussian-98 [21] revision A9 package without any symmetry restriction. Lowest energy conformers were located using Monte-Carlo method as implemented in Titan package version 1.0.5 [22]. The lowest energy conformers found were used as initial structures for the geometry optimization using Becke's parameter functional (B) [23] in combination with Lee, Yang and Parr (LYP) correlation function [24] and the 6-31G(d, p) standard basis set. The molecular geometries of the all calculated molecules were optimized to a global minimum at a B3LYP/6-31G(d, p) level of theory followed by frequency calculations at 298.15 K. All thermodynamic quantities were calculated by a standard statistical mechanical approach as implemented in the Gaussian 98 program. The equilibrium constants were calculated according to the Eq. (1).

$$\Delta G = -RT \ln K \quad (1)$$

where R is the universal gas constant, T the absolute temperature and ΔG the free Gibbs energy reaction

difference. The equilibrium concentrations of *trans*-, *trans,trans*- $C_{15}H_{24}$, *trans,trans,trans*- $C_{12}H_{18}$, *cis*- and *trans*- $C_{12}H_{20}$, *cis*- and *trans*- $C_{10}H_{16}$, *cis,cis*- $C_{10}H_{16}$, *cis*-*cis*- C_8H_{12} , *cis*- and *trans*- C_6H_{12} , 2-methyl-1,5-hexadiene (C_7H_{12}), 1,5-hexadiene (C_6H_{10}) and ethylene molecules were calculated assuming the equilibriums shown in Table 4 solving the following systems of equations (*trans*- and *cis*- have been abbreviated to *t*- and *c*-, respectively):

$$\begin{aligned} [C_7H_{12}]^5 / ([ttt-C_{15}H_{24}][c-C_{12}H_{20}][C_2H_4]^4) &= K1 \\ [C_7H_{12}] + [ttt-C_{15}H_{24}] + [c-C_{12}H_{20}] + [C_2H_4] &= 1 \\ [C_7H_{12}]^2 / ([c-C_{12}H_{20}][C_2H_4]) &= K2 \\ [C_7H_{12}]^2 / ([t-C_{12}H_{20}][C_2H_4]) &= K3 \\ [C_7H_{12}] + [C_{12}H_{20}] + [C_2H_4] &= 1 \\ [C_7H_{12}]^4 / ([cc-C_{10}H_{16}][c-C_{12}H_{20}][C_2H_4]^3) &= K4 \\ [C_7H_{12}] + [cc-C_{10}H_{16}] + [c-C_{12}H_{20}] + [C_2H_4] &= 1 \\ [C_6H_{10}]^5 / ([ttt-C_{12}H_{18}][t-C_{10}H_{16}][C_2H_4]^4) &= K5 \\ [C_6H_{10}] + [ttt-C_{12}H_{18}] + [t-C_{10}H_{16}] + [C_2H_4] &= 1 \\ [C_6H_{10}]^2 / ([t-C_{10}H_{16}][C_2H_4]) &= K6 \\ [C_6H_{10}]^2 / ([c-C_{10}H_{16}][C_2H_4]) &= K7 \\ [C_6H_{10}] + [C_{10}H_{16}] + [C_2H_4] &= 1 \end{aligned} \quad (2)$$

where K_1 – K_7 are respective equilibrium constants.

3. Results and discussion

Ethenolysis of 1,4-PI proceeds via intra- and inter-molecular routes to form a set of cyclic and linear oligomers. These products in the final stage will consist from linear molecules with one, two and more isoprene units and the all *trans* cyclic trimer as more thermodynamically favored among the all cyclic molecules [4,5]. Fig. 2 presents the possible distributions of products for the ethenolysis of 1,4-PI. Table 1 shows the calculated thermodynamic parameters of cyclic and linear molecules for the degradation of 1,4-PI and 1,4-PB via ethenolysis. As can see the possibility of the formation of *cis* and *trans* isoprene linear oligomers is practically same, while the formation of *trans* butadiene

oligomers becomes more preferable compared to *cis* isomers [5]. The identical standard energy terms for the isoprene molecules are due to the effect of the methyl substituents [4]. The calculated minimum energy conformations for the *cis* and *trans* isoprene oligomers (C₁₂H₂₀) are presented in Fig. 3. Table 2 presents the calculated standard free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) differences of chain-ring and chain-chain equilibrium for the ethenolysis of 1,4-PI and 1,4-PB. It follows from Table 2 that the depolymerization of the all-*trans* cyclic trimer (ttt-C₁₅H₂₄) and α,ω -vinyl-terminated isoprene molecules (entries 1 and 2) in the presence of ethylene to monomeric 2-methyl-1,5-hexadiene is thermodynamically very favored. (Fig. 4). This equilibrium for the cyclic isoprene dimer (cc-C₁₀H₁₆) is

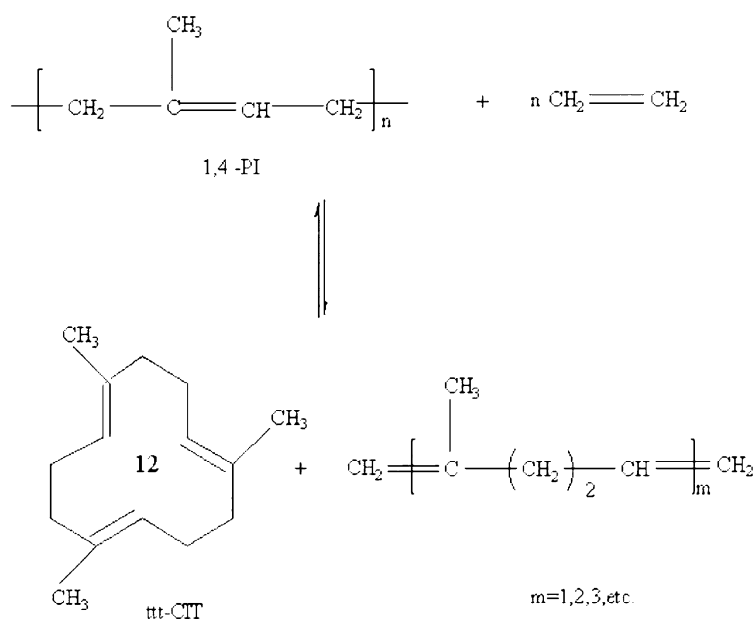


Fig. 2. Ethenolysis of 1,4-PI.

Table 1

Calculated standard free energy (G), enthalpy (H) and entropy (S) of cyclic and linear molecules for the ethenolysis of 1,4-PI and 1,4-PB at 25 °C

Compound	Formula	G	H	S
		kcal mol ⁻¹	kcal mol ⁻¹	cal mol ⁻¹ K
<i>cc</i> -CID ^a	C ₁₀ H ₁₆	-245030.3959	-245000.9858	98.6
<i>Ttt</i> -CIT ^a	C ₁₅ H ₂₄	-367554.630	-367516.2010	128.9
<i>Ttt</i> -CDT ^a	C ₁₂ H ₁₈	-293580.7789	-293548.9378	106.8
<i>c</i> -2,6-DM-1,5,9-decatriene ^b	C ₁₂ H ₂₀	-294334.4586	-294297.0797	125.4
<i>t</i> -2,6-DM-1,5,9-decatriene ^b	C ₁₂ H ₂₀	-294334.3456	-294297.3972	123.9
<i>c</i> -1,5,9-Decatriene	C ₁₀ H ₁₆	-245018.9576	-244986.3089	109.5
<i>t</i> -1,5,9-Decatriene	C ₁₀ H ₁₆	-245021.1294	-244987.9900	111.2
2-Methyl-1,5-hexadiene	C ₇ H ₁₂	-171818.8387	-171791.6625	91.2
1,5-Hexadiene	C ₆ H ₁₀	-147160.8014	-147135.9394	83.4
<i>c</i> -3-Methyl-2-pentene	C ₆ H ₁₂	-147928.8491	-147902.9430	86.9
<i>t</i> -3-Methyl-2-pentene	C ₆ H ₁₂	-147929.1020	-147903.0780	87.3
Ethylene	C ₂ H ₄	-49299.7881	-49283.7772	53.7

^a CID, CIT and CDT are the cyclic isoprene dimer, trimer and cyclic butadiene trimer, respectively.

^b 2,6-Dimethyl-1,5,9-decatriene.

completely shifted to 2-methyl-1,5-hexadiene (entry 3, Table 2, Fig. 5). It means that no cyclic dimers are formed during the ethenolysis of 1,4-PI and ring-opening cross metathesis of cyclic isoprene dimer with ethylene will result with high selectivity to 2-methyl-1,5-hexadiene. The calculations show that the possibility of the formation of cyclic oligomers for the ethenolysis of 1,4-PI is very small and equilibrium only exists between linear isoprene molecules and ethylene. The values of standard free energy differences for the ethenolysis of *cis* and *trans* isoprene oligomers to monomeric diene are the same (entries 4 and 5, Table 2, Fig. 6). Table 2 also shows that butadiene oligomers-1,5-hexadiene equilibrium is shifted toward the formation of the monomeric diene [5] (Fig. 7 and 8). Table 3 (entries 1–4) presents the values of ΔG and equilibrium constants for the depolymerization of isoprene oligomers to 2-methyl-1,5-hexadiene. It follows from Table 3 that natural rubber

and *trans*-PI will depolymerize to monomeric diene with same selectivity. Thus, the expected 2-methyl-1,5-hexadiene was detected during the ethenolysis of *trans*-PI by a tungsten carbene catalyst [20]. The use of high active and long-lived metathesis catalysts will result with high selectivity to monomeric 2-methyl-1,5-hexadiene. Table 3 (entries 5–7) shows the equilibrium constants for the ethenolysis of butadiene oligomers to 1,5-hexadiene. It is well known that the metathesis degradation of *cis*-PB to oligomers is accompanied by *cis-trans* isomerization to approach the equilibrium *trans/cis* ratio (about 80/20) [6,12,13]. Molecular modeling reveals that the low stereoselectivity for the metathesis of disubstituted olefins is due to the close matching of activation energies for the *cis* and *trans* isomer formation and the fast *cis-trans* isomerization by catalyst leading to equilibrium mixture of the isomers [25]. Early investigations for the *cis-trans* isomerization of *cis*-PB and

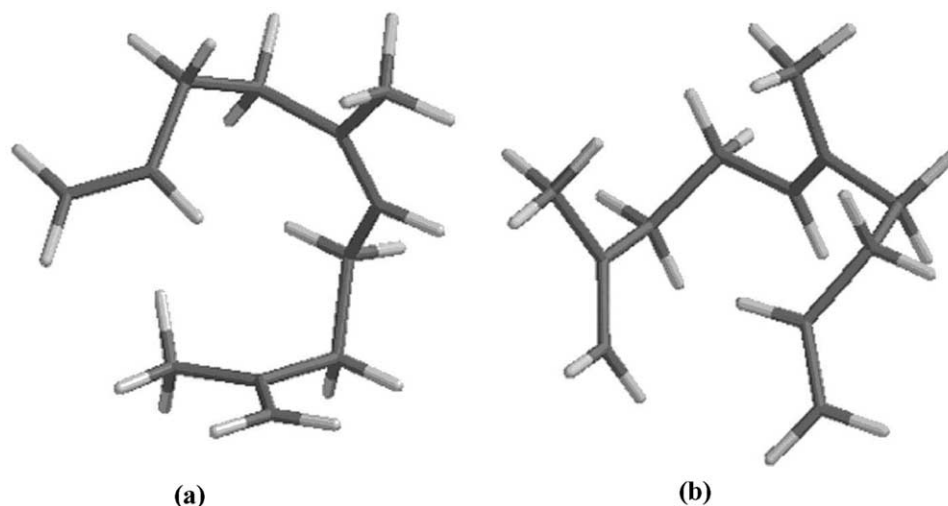


Fig. 3. Lowest energy conformers for *cis*- (a) and *trans*- (b) 2,6-dimethyl-1,5,9-decatriene ($C_{12}H_{20}$).

Table 2

Standard free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) differences of chain–ring and chain–chain equilibrium for the ethenolysis of 1,4-PI and 1,4-PB at 25 °C

Entry	Reaction	ΔG	ΔH	ΔS
		kcal mol ⁻¹	kcal mol ⁻¹	cal mol ⁻¹ K
1	<i>ttt</i> - $C_{15}H_{24}$ + <i>c</i> - $C_{12}H_{20}$ + 4 C_2H_4 \rightleftharpoons 5 $C_7H_{12}^a$	-6.0	-10	-13.1
2	<i>ttt</i> - $C_{15}H_{24}$ + <i>t</i> - $C_{12}H_{20}$ + 4 C_2H_4 \rightleftharpoons 5 $C_7H_{12}^a$	-6.0	-10	-12.6
3	<i>cc</i> - $C_{10}H_{16}$ + <i>t</i> - $C_{12}H_{20}$ + 3 C_2H_4 \rightleftharpoons 4 $C_7H_{12}^b$	-11.1	-17.3	-20.3
4	<i>c</i> - $C_{12}H_{20}$ + C_2H_4 \rightleftharpoons 2 $C_7H_{12}^c$	-3.4	-2.5	3.3
5	<i>t</i> - $C_{12}H_{20}$ + C_2H_4 \rightleftharpoons 2 $C_7H_{12}^c$	-3.5	-2.1	4.8
6	<i>ttt</i> - $C_{12}H_{18}$ + <i>t</i> - $C_{10}H_{16}$ + 4 C_2H_4 \rightleftharpoons 5 $C_6H_{10}^d$	-3.0	-7.7	-15.8
7	<i>c</i> - $C_{10}H_{16}$ + C_2H_4 \rightleftharpoons 2 $C_6H_{10}^e$	-3.0	-1.8	3.6
8	<i>t</i> - $C_{10}H_{16}$ + C_2H_4 \rightleftharpoons 2 $C_6H_{10}^e$	-0.7	-0.1	2.0

^a Fig. 4.

^b Fig. 5.

^c Fig. 6.

^d Fig. 7.

^e Fig. 8.

cis-PI using free radical initiators have demonstrated that equilibrium *cis/trans* content for the 1,4-PB is 25/75 at 25 °C, while this equilibrium for the 1,4-PI and 3-methyl-2-pentene corresponded to 45/55 [26,27]. The *cis-trans* isomerizations of 3-methyl-2-pentene have been studied using TiCl_4 , $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$ and $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ initiators [28]. The equilibrium *cis-trans* ratio in the monomer after the reaction was 42/58. In this study, we have analyzed the equilibrium *cis/trans* ratio for the 3-methyl-2-pentene using the DFT calculations. The cal-

culated *cis/trans* equilibrium constant for the 3-methyl-2-pentene is 1.7 (entry 8, Table 3) which corresponds to 40 mol% of *cis* and 60 mol% of *trans* double bonds. As can see this value is very close to the experimentally observed [26–28]. Fig. 9 presents the calculated minimum energy conformations for the *cis* and *trans* isomers of 3-methyl-2-pentene. It has been reported that *cis*-PI in the presence of terminal olefins as CTAs degraded by a high stable tungsten-containing catalyst to oligomers which still mainly contain *cis* double bonds [18,29].

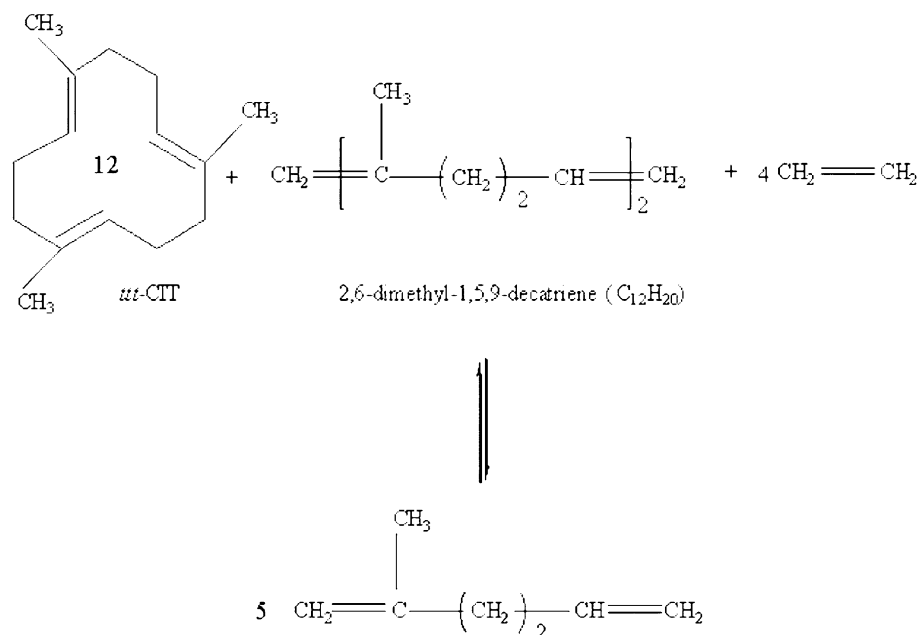


Fig. 4. Equilibrium between all-*trans* cyclic trimer, 2,6-dimethyl-1,5,9-decatriene ($\text{C}_{12}\text{H}_{20}$) and 2-methyl-1,5-hexadiene for the ethenolysis of 1,4-PI.

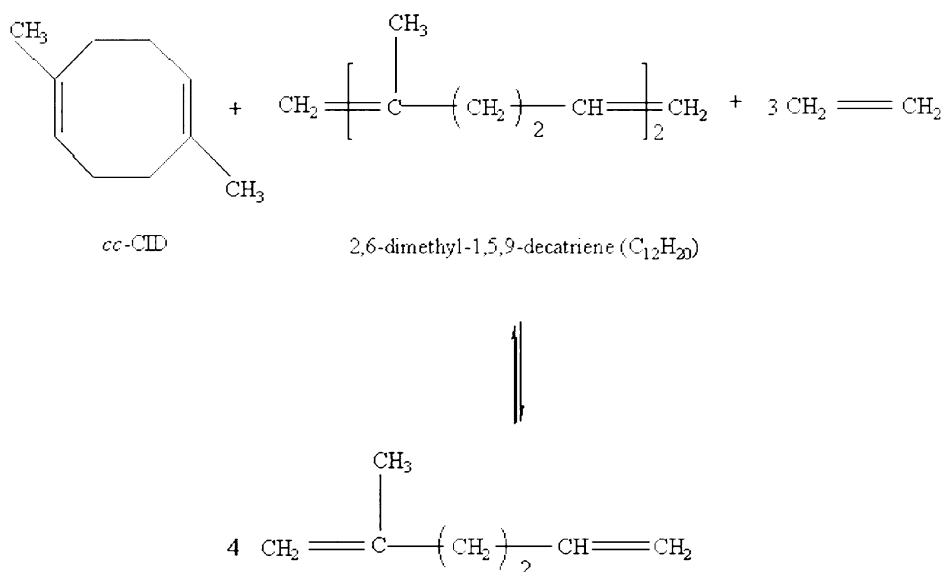


Fig. 5. Ethenolysis of cyclic isoprene dimer (*cc*- $\text{C}_{10}\text{H}_{16}$) and 2,6-dimethyl-1,5,9-decatriene to 2-methyl-1,5-hexadiene.

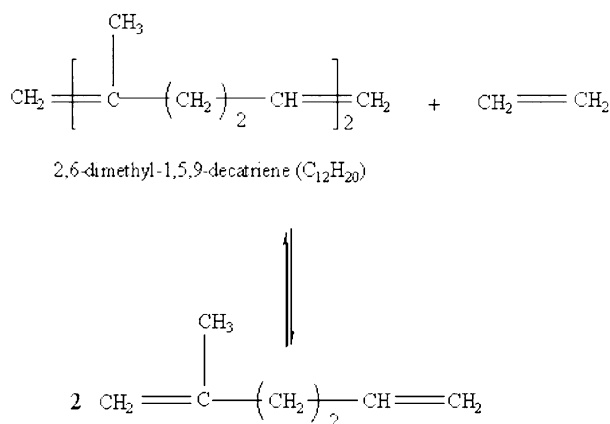


Fig. 6. Ethenolysis of 2,6-dimethyl-1,5,9-decatriene (C₁₂H₂₀) to 2-methyl-1,5-hexadiene.

Table 4 lists the calculated distributions of cyclic and linear molecules for the ethenolysis of 1,4-PI and 1,4-PB. It is seen that this reaction for the 1,4-PI is completely shifted to 2-methyl-1,5-hexadiene. The concentration of the monomeric diene at equilibrium with linear oligomers is of 90 mol%. According to the calculations, ethenolysis of *trans,trans,trans*-1,5,9-trimethyl-1,5,9-cyclododecatriene (*ttt*-C₁₅H₂₄) and *cis,cis*-1,5-dimethyl-1,5-cyclooctadiene (*cc*-C₁₀H₁₆) to 2-methyl-1,5-hexadiene is thermodynamically very favored and proceeds with high selectivity. As seen from Table 4 the concentration of 1,5-hexadiene at equilibrium with butadiene oligomers is of 46 mol%. The results of calculations are in agreement with experimental data obtained for the ethenolysis of *cis,cis*-1,5-cyclooctadiene (COD) by rhenium based catalysts [30] and *cis*-PB using a well-defined ruthenium alkylidene catalyst [3]. It should be noted that the acyclic diene metathesis oligomerization (ADMET) of 1,5-hexadiene again producing butadiene

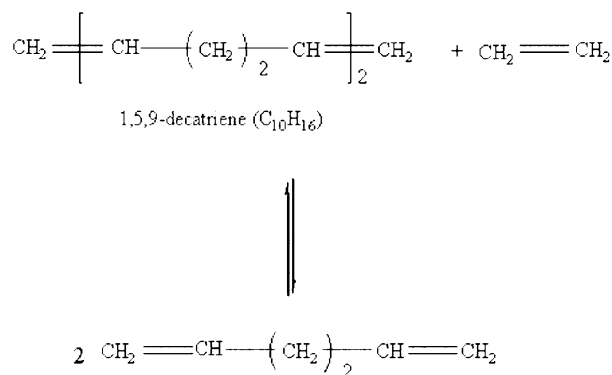


Fig. 8. Ethenolysis of 1,5,9-decatriene (C₁₀H₁₆) to 1,5-hexadiene.

Table 3

Calculated standard free energy (ΔG) and equilibrium constant (K) of the chain–ring and chain–chain equilibrium for the ethenolysis of 1,4-PI and 1,4-PB at 25 °C

Entry	Reaction	ΔG	K
		kcal mol ⁻¹	
1	<i>ttt</i> -C ₁₅ H ₂₄ + <i>t</i> -C ₁₂ H ₂₀ + 4 C ₂ H ₄ ⇌ 5 C ₇ H ₁₂ ^a	-6.0	25 × 10 ³
2	<i>cc</i> -C ₁₀ H ₁₆ + <i>t</i> -C ₁₂ H ₂₀ + 3 C ₂ H ₄ ⇌ 4 C ₇ H ₁₂ ^b	-11.1	14 × 10 ⁷
3	<i>c</i> -C ₁₂ H ₂₀ + C ₂ H ₄ ⇌ 2 C ₇ H ₁₂ ^c	-3.4	312
4	<i>t</i> -C ₁₂ H ₂₀ + C ₂ H ₄ ⇌ 2 C ₇ H ₁₂ ^c	-3.5	368
5	<i>ttt</i> -C ₁₂ H ₁₈ + <i>t</i> -C ₁₀ H ₁₆ + 4 C ₂ H ₄ ⇌ 5 C ₆ H ₁₀ ^d	-3.0	164
6	<i>c</i> -C ₁₀ H ₁₆ + C ₂ H ₄ ⇌ 2 C ₆ H ₁₀ ^e	-3.0	164
7	<i>t</i> -C ₁₀ H ₁₆ + C ₂ H ₄ ⇌ 2 C ₆ H ₁₀ ^e	-0.7	3
8 ^f	<i>c</i> -C ₆ H ₁₂ ⇌ <i>t</i> -C ₆ H ₁₂ ^g	-0.3	1.7

^a Fig. 4.

^b Fig. 5.

^c Fig. 6.

^d Fig. 7.

^e Fig. 8.

^f ΔG for the equilibrium of isomers calculated using B3LYP/6-311G(2d,p) was -0.4 kcal/mol.

^g Fig. 9.

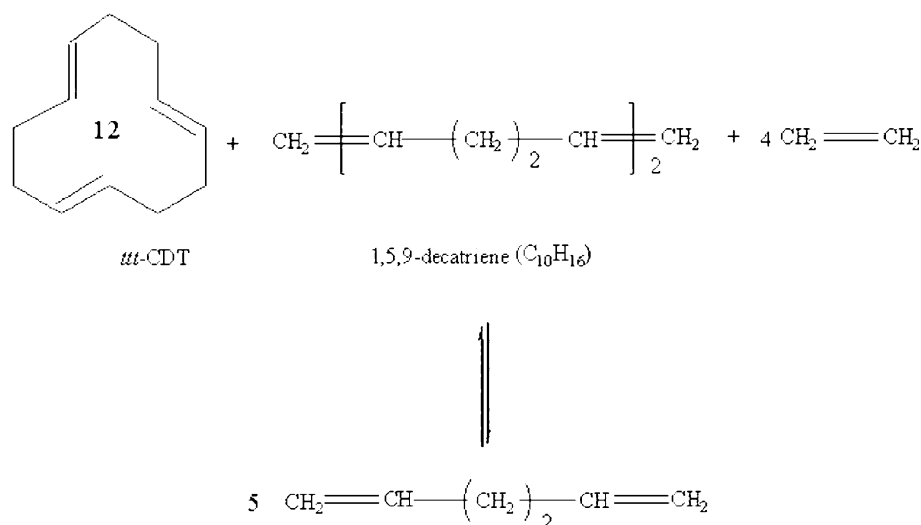


Fig. 7. Equilibrium between all-*trans* cyclic trimer, 1,5,9-decatriene (C₁₀H₁₆) and 1,5-hexadiene for the ethenolysis of 1,4-PB.

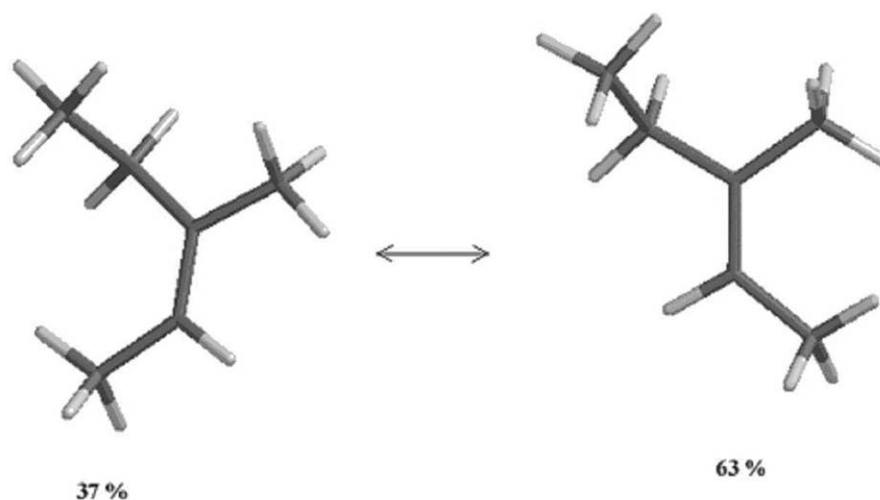


Fig. 9. Equilibrium between lowest energy conformers of *cis*- and *trans*-3-methyl-2-pentene (C_6H_{12}).

Table 4

Calculated cyclic and linear molecules distributions for the ethenolysis of 1,4-PI and 1,4-PB at 25 °C

Reaction	mol%			
	<i>ttt</i> - $C_{15}H_{24}$ (<i>ttt</i> - $C_{12}H_{18}$)	$C_{12}H_{20}$ ($C_{10}H_{16}$)	C_2H_4	C_7H_{12} (C_6H_{10}) ^a
<i>Ttt</i> - $C_{15}H_{24}$ + <i>t</i> - $C_{12}H_{20}$ + 4 C_2H_4 \rightleftharpoons 5 C_7H_{12} ^b	4	4	15	77
<i>cc</i> - $C_{10}H_{16}$ + <i>t</i> - $C_{12}H_{20}$ + 3 C_2H_4 \rightleftharpoons 4 C_7H_{12} ^c		1	15	83
<i>c</i> - $C_{12}H_{20}$ + C_2H_4 \rightleftharpoons 2 C_7H_{12} ^d		5	5	90
<i>t</i> - $C_{12}H_{20}$ + C_2H_4 \rightleftharpoons 2 C_7H_{12} ^d		5	5	90
<i>Ttt</i> - $C_{12}H_{18}$ + <i>t</i> - $C_{10}H_{16}$ + 4 C_2H_4 \rightleftharpoons 5 C_6H_{10} ^e	9	9	36	46
<i>t</i> - $C_{10}H_{16}$ + C_2H_4 \rightleftharpoons 2 C_6H_{10} ^f		27	27	46

^a The values of experimentally observed yield of 1,5-hexadiene (C_6H_{10}) for the ethenolysis of COD (ethylene/COD = 2) [30] and *cis*-PB (30 psig C_2H_4 pressure) [3] are 50 and 43 mol%, respectively.

^b Fig. 4.

^c Fig. 5.

^d Fig. 6.

^e Fig. 7.

^f Fig. 8.

oligomers proceeded more easily than that for the 2-methyl-1,5-hexadiene to isoprene oligomers. Thus, equilibrium constants for the depolymerization of butadiene and isoprene oligomers to monomeric dienes are 3 and 312, respectively (Table 3, entries 2, 3 and 7). The calculations show that the selective depolymerization of 1,4-PI to monomeric diene can be realized without the need of high excess of ethylene.

4. Conclusions

According to the calculations, equilibrium of cyclic and linear isoprene molecules for the ethenolysis of 1,4-PI is completely shifted to 2-methyl-1,5-hexadiene. The

amounts of cyclic isoprene dimers (*cc*- $C_{10}H_{16}$) and trimers (*ttt*- $C_{15}H_{24}$) in equilibrium with linear oligomers are negligible. The concentration of 2-methyl-1,5-hexadiene at equilibrium with α,ω -vinyl-terminated isoprene oligomers is high and corresponds to 90 mol%. Therefore, natural rubber and *trans*-PI in the presence of linear olefins as CTAs will copolymerize by active and long-lived metathesis catalysts to monomeric diene with high selectivity. In the case of 1,4-PB ethenolysis, the concentration of 1,5-hexadiene at equilibrium with butadiene molecules corresponds to 46 mol%. The calculations show that equilibrium *cis/trans* ratio for the isoprene and butadiene oligomers is different. According to the calculations and experimental data, equilibrium *cis/trans* ratio in disubstituted olefins is 20/80,

while this value for the trisubstituted olefins corresponds to 40/60. It follows from calculations that ring-opening cross metathesis of cyclic isoprene dimer (*cc*-C₁₀H₁₆) and trimer (*ttt*-C₁₅H₂₄) with ethylene will result with high selectivity to 2-methyl-1,5-hexadiene.

Acknowledgements

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