

Computational study of metathesis degradation of rubber, 1

Distribution of cyclic oligomers via intramolecular metathesis degradation of *cis*-polybutadiene

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(Received: June 7, 1999; revised: July 12, 1999)

SUMMARY: The results of the molecular modelling of the intramolecular metathesis degradation of *cis*-polybutadiene (*cis*-PB) into cyclic oligomers at PM3 level of theory showed that the chain-ring equilibrium is completely shifted towards the all-*trans* cyclic isomers. The formation of cyclic products, containing from three to six butadiene units, from larger rings is thermodynamically favoured with cyclic butadiene tetramers and pentamers being the main products. These results are in reasonable agreement with most of the available experimental data. The discrepancy observed in some cases between found and calculated ring distributions for the intramolecular metathesis degradation of *cis*-PB suggests that the reaction is kinetically controlled under certain conditions.

Introduction

One of the main features of the metathesis of linear and cyclic olefins is that the total number and types of the chemical bonds are conserved during the reaction. Since the metathesis reaction can be carried out by selective and highly stable catalysts in a broad temperature range, very reliable thermodynamic data about the products distribution can be obtained. Thus, the equilibrium distribution of the alkylidene moieties was calculated for the metathesis of simple linear olefins^{1,2}.

The double bonds of formed polymer chains participate in the intramolecular degradation by the same carbene mechanism³ during the ring-opening metathesis polymerisation of cycloolefins (ROMP) resulting in the formation of cyclic oligomers with the molecular masses being multiples of the starting monomer^{4–6} (Fig. 1). The ring-opening of cycloolefins generally takes place with a significant thermal effect and is considerably more rapid than the intramolecular degradation giving oligomeric rings. However, the rate of polymer chain cyclodegradation increases with the degree of polymerisation producing oligomers with very broad molecular weight distribution (MWD). The formation of high molecular weight polymer depends on the initial monomer concentration in solution. When the initial monomer concentration is below critical only cyclooligomers are found in the reaction mixture^{5,6}.

Many studies have been made on the metathesis degradation of rubber^{7,8}. The intramolecular metathesis degradation of many polyalkenamers^{9,10} and its co-metathesis with linear olefins as chain transfer agents^{11–15} using

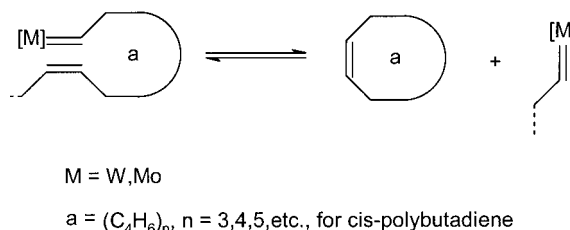


Fig. 1. Intramolecular degradation via metathesis

tungsten and molybdenum based metathesis catalysts have been carried out to produce low molecular weight and end-functionalised oligomers.

The intramolecular reaction rapidly reaches equilibrium at room temperature. In the case of the W-containing catalyst the intramolecular degradation is accompanied by a gradual *cis-trans* isomerization^{6–10}, while MoCl₃[OCO(CH₂)₁₆CH₃]₂-R₂AlCl-catalyst does not change the *cis*-configuration of the double bonds of the obtained oligomers¹⁶. Detailed investigations of the intramolecular degradation show that the composition of cyclic oligomers depends on the double bond distribution in the polymer chain and the polymer-cyclooligomers equilibrium is independent of the reaction temperature in a certain temperature range^{17,18} in contrast to the polypentenamer-cyclopentene equilibrium^{19,20}. If the formation of cyclics is thermodynamically favoured, the intramolecular degradation will completely be shifted towards these cyclic oligomers. The ROMP of 1,5-cyclooctadiene and the intramolecular degradation of *cis*-PB by W-containing catalysts reaches the equilibrium (the addition of fresh catalyst does not change the oligomeric distributa-

tion) giving a set of cyclic butadiene tetramers and pentamers as main products^{6, 17, 21–23}. On the other hand, kinetic studies of the ROMP of 1,5-cyclooctadiene and the intramolecular degradation of *cis*-PB using the stable tungsten carbene complex demonstrated that the formation of butadiene trimers is highly favoured²⁴.

The goal of the present study is to examine the thermodynamic aspects of the intramolecular metathesis degradation of *cis*-PB using quantum chemistry tools and to compare the experimental results with theoretical calculations.

Methods

All calculations were performed using Gaussian-98²⁵; initial geometries were generated using CS Chem3D Pro Version 4.0 after preliminary optimisation with MM2 force field²⁵. First, the molecular geometries of all isomers of 1,5-cyclooctadiene (COD) and cyclododecatriene (CDT) were optimised to a local minimum at PM3 and RHF/3-21G levels of theory followed by the frequency calculations to reach thermodynamic parameters. Both calculations gave very similar results, therefore the PM3 model Hamiltonian was chosen as the computationally less demanding alternative. All molecular geometries were optimised to a local minimum at PM3 level of theory followed by frequency calculations at 298.15 K to calculate Gibbs free energy.

A *cis*-oligobutadiene molecule containing 13 butadiene units with terminal hydrogen atoms was used as a model of the *cis*-PB chain (Fig. 2). The equilibrium constants were calculated according to

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

where R is the universal gas constant, T the absolute temperature and ΔG the free Gibbs energy reaction difference. The equilibrium concentrations of all-*trans* C₁₂H₁₈, C₁₆H₂₄, C₂₀H₃₀ and C₂₄H₃₆ molecules were calculated assuming the equilibrium shown in Fig. 3 solving the following system of equations:

$$\begin{aligned} \frac{[\text{C}_{16}\text{H}_{24}]^{15}}{[\text{C}_{12}\text{H}_{18}]^{20}} &= K_1 \\ \frac{[\text{C}_{16}\text{H}_{24}]^{15}}{[\text{C}_{20}\text{H}_{30}]^{12}} &= K_2 \\ \frac{[\text{C}_{20}\text{H}_{30}]^{12}}{[\text{C}_{24}\text{H}_{36}]^{10}} &= K_3 \\ \frac{[\text{C}_{24}\text{H}_{36}]^{10}}{[\text{C}_{12}\text{H}_{18}]^{20}} &= K_4 \\ \frac{[\text{C}_{24}\text{H}_{36}]^{10}}{[\text{C}_{16}\text{H}_{24}]^{15}} &= K_5 \\ \frac{[\text{C}_{20}\text{H}_{30}]^{12}}{[\text{C}_{12}\text{H}_{18}]^{20}} &= K_6 \\ [\text{C}_{12}\text{H}_{18}] + [\text{C}_{16}\text{H}_{24}] + [\text{C}_{20}\text{H}_{30}] + [\text{C}_{24}\text{H}_{36}] &= 1 \end{aligned} \quad (2)$$

where K are the respective equilibrium constants.

Results and discussion

It has been shown that the active carbene species formed on the polymer chain can completely degrade the polymer molecule in dilute solution to form a variety of cyclic

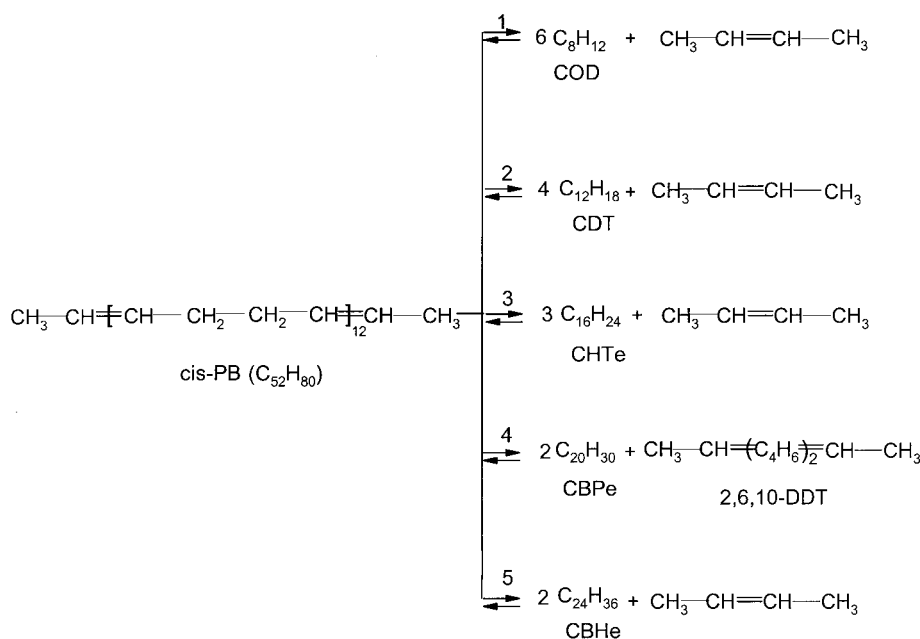
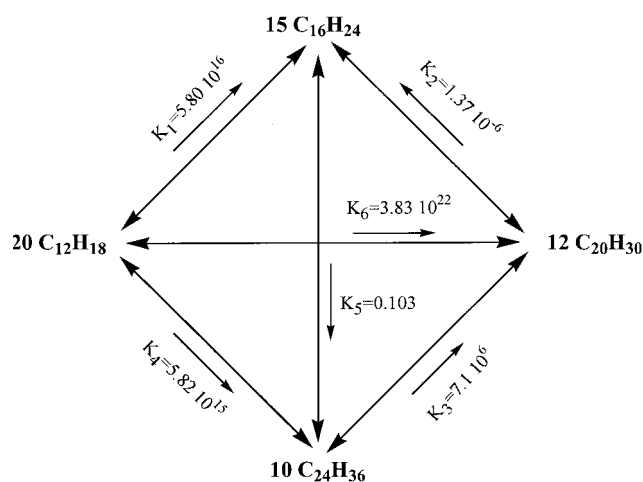


Fig. 2. Intramolecular metathesis degradation of *cis*-PB to cyclooligomers

Fig. 3. Equilibrium between all-*trans* cyclic oligomers

oligomers^{6,21}). Fig. 2 illustrates a possible oligomeric ring distribution for the metathesis cyclodegradation of *cis*-PB. It should be noted that first, the Gibbs energy (ΔG), the enthalpy (ΔH) and the entropy (ΔS) differences of the intramolecular metathesis degradation of *cis*-PB into cyclooligomers with different double bond configurations were calculated for the simple chain-ring equilibrium (Fig. 2). Tab. 1 shows the calculated thermodynamic parameters of model *cis*-PB and the oligomeric molecules. Tab. 2 presents theoretical ΔG , ΔH and ΔS for the *cis*-PB-rings equilibrium according to Fig. 2. The results show that the cyclic all-*trans*-isomers (except COD) are more stable compared to the corresponding *cis*-isomers. The formation of cc-COD via intramolecular degradation

Tab. 1. Calculated Gibbs free energy (G), enthalpy (H) and entropy (S) for cyclic and linear products of the intramolecular degradation of *cis*-PB at 298.15 K

Compound	Formula	G	H	S
		kcal · mol ⁻¹		cal · mol ⁻¹ · K ⁻¹
<i>cis</i> -PB	C ₅₂ H ₈₀	714.5	819.5	352.0
cc-COD	C ₈ H ₁₂	108.1	133.0	82.8
ccc-CDT	C ₁₂ H ₁₈	162.9	192.0	97.6
cct-CDT	C ₁₂ H ₁₈	165.9	197.3	102.0
ctt-CDT	C ₁₂ H ₁₈	163.4	195.1	106.5
ttt-CDT	C ₁₂ H ₁₈	162.4	195.4	110.8
cccc-CHTe	C ₁₆ H ₂₄	219.0	257.4	128.8
ccct-CHTe	C ₁₆ H ₂₄	216.7	254.9	128.3
cctt-CHTe	C ₁₆ H ₂₄	216.6	256.4	133.3
ctct-CHTe	C ₁₆ H ₂₄	217.4	257.0	132.9
cttt-CHTe	C ₁₆ H ₂₄	215.8	255.1	131.9
tttt-CHTe	C ₁₆ H ₂₄	214.9	256.2	138.4
ttttt-CBPe ^{a)}	C ₂₀ H ₃₀	268.0	315.9	160.5
tttttt-CBHe ^{a)}	C ₂₄ H ₃₆	322.6	381.0	196.1
ttttttt-CBHp ^{a)}	C ₂₈ H ₄₂	378.8	441.3	209.9
tttttttt-CBE ^{a)}	C ₃₂ H ₄₈	440.1	506.9	223.9
ttt-2,6,10-DDT ^{a)}	C ₁₂ H ₂₀	154.8	193.9	131.4
c-butene	C ₄ H ₈	46.4	67.8	71.6
t-butene	C ₄ H ₈	45.5	67.3	73.2

^{a)} Calculated only for all-*trans* isomers; CBPe, CBHe, CBHp, CBE are cyclic oligomers containing 5, 6, 7 and 8 butadiene units, respectively.

of *cis*-PB is thermodynamically favoured. The formation of small amounts of COD during the cyclodegradation of *cis*-PB has been reported earlier⁸). In Tab. 3 are listed the calculated ΔG and the equilibrium constant (K) for the *cis*-PB-cyclic oligomers equilibrium.

Tab. 2. Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) differences for *cis*-PB-cyclic oligomer equilibrium at 298.15 K

Cis-polybutadiene – ring equilibrium		ΔG	ΔH	ΔS
		kcal · mol ⁻¹		cal · mol ⁻¹ · K ⁻¹
<i>cis</i> -PB →	6 cc-COD + c-butene ^{a)}	-19.8	44.8	216.6
	6 cc-COD + t-butene ^{a)}	-20.7	44.4	218.3
	4 ccc-CDT + c-butene ^{b)}	-16.5	16.3	110.1
	4 ccc-CDT + t-butene ^{b)}	-17.4	15.9	111.8
	4 cct-CDT + c-butene ^{b)}	-4.3	33.8	127.5
	4 cct-CDT + t-butene ^{b)}	-5.1	33.3	129.4
	4 ctt-CDT + c-butene ^{b)}	-14.5	28.9	145.7
	4 ctt-CDT + t-butene ^{b)}	-15.5	28.5	147.4
	4 ttt-CDT + c-butene ^{b)}	-18.6	28.9	162.8
	4 ttt-CDT + t-butene ^{b)}	-19.6	29.5	164.4
	3 tttt-CHTe + t-butene ^{c)}	-24.2	16.6	136.7
2 ttttt-CBPe + ttt-2,6,10-DDT ^{d)}	-23.7	6.2	100.4	
2 tttttt-CBHe + t-butene ^{e)}	-23.9	9.9	113.4	

^{a)} Route 1, Fig. 2.

^{b)} Route 2, Fig. 2.

^{c)} Route 3, Fig. 2.

^{d)} Route 4, Fig. 2.

^{e)} Route 5, Fig. 2.

Tab. 3. Calculated ΔG and the equilibrium constant (K) of the chain-ring and ring-ring equilibrium for the intramolecular metathesis degradation of *cis*-PB at 298.15 K

Reaction	ΔG kcal/mol	K
$C_{52}H_{80} \rightleftharpoons ttt-C_{12}H_{18} + tttt-C_{16}H_{24} + ttttt-C_{20}H_{30} + t-C_4H_8$	-23.7	2.30×10^{17}
$C_{52}H_{80} \rightleftharpoons ttttt-C_{20}H_{30} + tttttt-C_{28}H_{42} + t-C_4H_8$	-22.2	2.0×10^{16}
$C_{52}H_{80} \rightleftharpoons ttttttt-C_{32}H_{48} + tttt-C_{16}H_{24} + t-C_4H_8$	-13.7	1.45×10^{10}
$2 ttttttt-C_{32}H_{48} + tttttt-C_{28}H_{42} \rightleftharpoons ttt-C_{12}H_{18} + tttt-C_{16}H_{24} + 2 ttttt-C_{20}H_{30} + tttttt-C_{24}H_{36}$	-23.2	1.05×10^{17}
$9 cc-C_8H_{12} \rightleftharpoons ttt-C_{12}H_{18} + tttt-C_{16}H_{24} + ttttt-C_{20}H_{30} + tttttt-C_{24}H_{36}$	-4.6	2300
$10 cc-C_8H_{12} \rightleftharpoons tttt-C_{16}H_{24} + 2 ttttt-C_{20}H_{30} + tttttt-C_{24}H_{36}$	-6.5	60000
$5 ttt-C_{12}H_{18} \rightleftharpoons tttt-C_{16}H_{24} + ttttt-C_{20}H_{30} + tttttt-C_{24}H_{36}$	-6.3	40000
$5 tttt-C_{16}H_{24} \rightleftharpoons ttt-C_{12}H_{18} + ttttt-C_{20}H_{30} + 2 tttttt-C_{24}H_{36}$	0.8	0.3
$6 ttttt-C_{20}H_{30} \rightleftharpoons 4 ttt-C_{12}H_{18} + 3 tttt-C_{16}H_{24} + tttttt-C_{24}H_{36}$	8.7	4.1×10^{-7}
$2 tttttt-C_{24}H_{36} \rightleftharpoons ttt-C_{12}H_{18} + tttt-C_{16}H_{24} + ttttt-C_{20}H_{30}$	0.2	0.7
$2 ccc-C_{12}H_{18} \rightleftharpoons 3 cc-C_8H_{12}$	-1.6	15
$2 ccc-C_{12}H_{18} \rightleftharpoons 3 cc-C_8H_{12}^a)$	-1.8	20

a) HF/3-21G/HF/3-21G level of theory.

It follows from the Tab. 3 that the oligomerisation of COD would produce $C_{16}H_{24}$, $C_{20}H_{30}$ and $C_{24}H_{36}$ cyclics rather than smaller $C_{12}H_{24}$ rings. The ROMP of *cc*-COD below the critical concentration leads to cyclic oligomers similar to those from the intramolecular metathesis degradation of *cis*-PB. It was demonstrated that the ROMP of COD by a classical tungsten-based catalyst yields only cyclic oligomers at concentrations below 8 wt.-% in toluene, while the polymerisation in more concentrated solution produces high molecular weight *cis*-PB. However, the addition of fresh catalyst to the reaction mixture causes a drastic reduction of the molecular weight to form cyclic oligomers with a molecular weight distribution similar to that for the intramolecular degradation of *cis*-PB^{6,9,17} proving that the ROMP is a kinetically controlled reaction. It is noteworthy that the critical monomer concentration depends on the nature of cycloolefins^{6,9}.

Tab. 3 shows that the chain-ring equilibrium is completely shifted towards the all-*trans* $C_{12}H_{18}$ – $C_{32}H_{48}$ cyclics. It is seen that the formation of all-*trans* isomers containing from three to six butadiene units from larger rings ($C_{28}H_{42}$ and $C_{32}H_{48}$) is thermodynamically favoured. When equilibrium is reached the all-*trans* cyclic butadiene trimers, tetramers, pentamers and hexamers will be the main products. Fig. 3 shows equilibrium between these cyclooligomers. As seen from Fig. 3 the equilibrium is shifted towards cyclic butadiene tetramers, pentamers and hexamers. The equilibrium distribution of the all-*trans* oligomeric products from the intramolecular metathesis degradation of *cis*-PB at 298.15 K (Tab. 4) according to Fig. 3 agrees reasonably with most of the available experimental data with the butadiene tetramers and pentamers being the main products^{6,17,21–23}. According to the calculations, the main product of the intramolecular metathesis degradation of *cis*-PB is the cyclic buta-

Tab. 4. Experimentally observed and calculated distribution of cyclic all-*trans* oligomers after intramolecular metathesis degradation of *cis*-PB

Compound	Mole fraction of oligomer in % ²⁴⁾	Mole fraction of oligomer in % ^{17,21)}	Calculated mole fraction of oligomer in %
$C_{12}H_{18}$	81.4	2	0
$C_{16}H_{24}$	5.4	28	28
$C_{20}H_{30}$	6.3	21	61
$C_{24}H_{36}$	4.0	15	11
$C_{28}H_{42}$	2.0	12	–

diene pentamer (61 mol-%) followed by tetramer (28 mol-%) and hexamer (11 mol-%). On the other hand, the calculated oligomeric distribution differs significantly from other experimental data²⁴⁾ (Tab. 4). The observed discrepancy can be explained by the fact that in this particular case the equilibrium state has not been reached.

Conclusions

The calculations demonstrated that the chain-rings equilibrium is completely shifted towards the all-*trans* cyclic butadiene tetramers and pentamers. The calculated equilibrium distribution of all-*trans* oligomeric products from the intramolecular metathesis degradation of *cis*-PB agrees reasonably with most of the available experimental data. The discrepancy between some of the determined and calculated cyclic product distributions for the intramolecular metathesis degradation of *cis*-PB can be explained by the fact that the chain-cyclic oligomers reaction is kinetically controlled under certain experimental conditions.

The oligomerisation of relatively small rings (COD and CDT) to products containing cyclic butadiene tetramers,

pentamers and hexamers is thermodynamically favoured. It suggests that the ROMP of these rings below critical concentrations produces cyclic oligomers similar to the intramolecular degradation of *cis*-PB.

Acknowledgement: This investigation was supported by a Grant from CONACyT with contract 03-76(0085P-B).

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