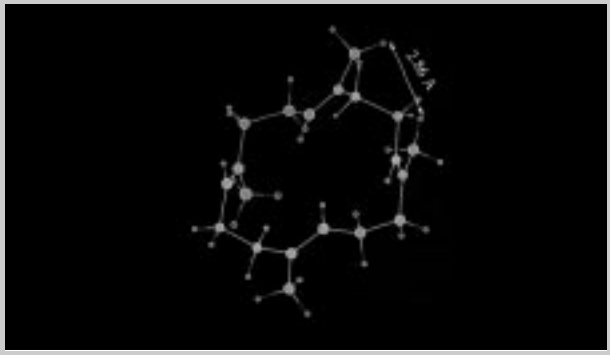
Full Paper: The results of molecular modeling of the ring distributions for the intramolecular metathesis degradation of natural rubber (NR) at HF/6–31G(d) level of theory showed that in the ring-ring equilibrium participate cyclic oligomers containing from two to four isoprene units with all-*trans* cyclic isoprene trimer being the main product. The formation of *trans,trans,trans*-1,5,9-trimethyl-1,5,9-cyclododecatriene from larger rings is thermodynamically favored. According to the calculations, the ring-ring equilibrium for the intramolecular metathesis degradation of *cis*-polybutadiene (*cis*-PB) is completely shifted towards the all-*trans* cyclic butadiene trimer. These results are in reasonable agreement with recent experimental data.



Lowest energy conformers located for all-*trans* cyclic isoprene tetramer ($C_{20}H_{32}$) using simulate annealing technique.

Computional Study of Metathesis Degradation of Rubber, 2[a]

Distribution of Cyclic Oligomers via Intramolecular Metathesis Degradation of Natural Rubber

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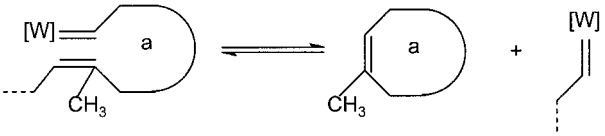
Introduction

The detailed investigations show that the intramolecular metathesis degradation of unsaturated polymers is a chain process[1, 2] and the reaction rapidly reaches equilibrium at room temperature to yield a set of cyclic oligomers (Figure 1). The composition of the cyclic products depends on the double bonds distribution in the polymer chain and the chain-ring equilibrium is independent of the reaction temperature in certain temperature range[3, 4] in contrast to polypentanamer-cyclopentene equlibrium.[5, 6]

There are many investigations on the metathesis degradation of synthetic rubber.[7] The intra- and intermolecular metathesis degradation of *cis*-polybutadiene (*cis*-PB) and other polyalkenamers have been performed using tungsten and molybdenum based metathesis catalysts.[2–4, 8–11]

On the other hand, very few reports are related to the metathesis degradation of natural rubber (NR).[12–15] This



a = $(C_5H_8)_n$, n =2, 3,4,5,etc.,

Figure 1. Intramolecular degradation of NR via metathesis.

may be due to the fact that NR is very sensitive to side reactions and, therefore, the classical catalysts based on tungsten chloride and molybdenum chloride cause the cationic cyclization and other side reactions. Thus, it has been shown that the degradation of NR using WCl_6—$Sn(CH_3)_4$ leads to a considerable decrease in the carbon-carbon double bonds content in the obtained products.[13] The authors[14, 15] demonstrated the importance of double bond shift in the degradation of NR by the

[a] Part 1, cf. ref.[17]

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WCI_6—$AIEtCI_2$ catalyst. It has been shown that the use of the extremely high stable $W[OCH(CH_2CI)_2]_2CI_4$—$Al(C_2H_5)_2CI$-anisole catalyst led to the efficient intra- and intermolecular metathesis degradation of *cis*-polyisoprene (PI) without any side reaction.[16] It is important to note that the addition of anisole to the catalyst makes it possible to degrade *cis*-PI into oligomeric products without a loss of unsaturation. According to the experimental results, the metathesis degradation of *cis*-PI in contrast to *cis*-PB proceeds very slowly and leads to the oligomers with predominant *cis*-configuration of the double bonds. Authors explained this phenomenon by steric effects of the methyl side chain group. It has been shown that the intramolecular degradation of *cis*-PI in dilute solution took more than 200 h to form cyclic oligomers.[16] The addition of fresh catalyst led to a slow drop of the molecular weight of oligomers.

In our previous paper it has been reported the results of molecular modeling of the intramolecular metathesis degradation of *cis*-PB to cyclic oligomers using PM3 semiempirical model.[17]

The purpose of the present study is to examine the oligomeric ring distribution for the intramolecular metathesis degradation of NR and *cis*-PB usingmore rigorous ab initio approach.

Methods

All geometry optimizations were carried out using Gaussian-98[18] revision A7 package without any symmetry restriction. Lowest energy conformers were located using the simulated annealing technique making use of the MM2 force field[19] Simulated annealing was carried out by running molecular dynamics at 1 000 K during 30 ps followed by slow (0.1 kcal/atom ps) cooling down the molecule to 0 K. The found lowest energy conformers were used as initial structures for HF/6–31G* optimizations. The molecular geometries of the all calculated molecules were optimized to a global minimum at RHF/6–31G* level of theory followed by frequency calculations at 298.15 K. All thermodynamic quantities were calculated by standard statistical mechanical approach as implemented in the Gaussian 98 program. The equilibrium constants were calculated according to Equation (1).

$$\Delta G = -RT\ln K \tag{1}$$

where R is universal gas constant, T the absolute temperature and ΔG the free Gibbs energy reaction difference. The equilibrium concentrations of *cis*,*cis*-$C_{10}H_{16}$, *trans*,*trans*-$C_{15}H_{24}$ and *cis*,*cis*,*cis*,*cis*-$C_{20}H_{32}$ isoprene molecules were calculated assuming the equilibrium shown in Figure 4 solving the following systems of equations:

$$\begin{aligned}
&[ttt\text{-}C_{15}H_{24}]^4/[cc\text{-}C_{10}H_{16}]^6 = K_1\\
&[cccc\text{-}C_{20}H_{32}]^3/[ttt\text{-}C_{15}H_{24}]^4 = K_2\\
&[cccc\text{-}C_{20}H_{32}]^3/[cc\text{-}C_{10}H_{16}]^6 = K_3\\
&[cc\text{-}C_{10}H_{16}] + [ttt\text{-}C_{15}H_{24}] + [cccc\text{-}C_{20}H_{32}] = 1
\end{aligned} \tag{2}$$

The equilibrium concentrations of the all-*trans* cyclic butadiene molecules were calculated assuming the equilibrium shown in Figure 6 solving the following system of equations:

$$\begin{aligned}
&[C_{16}H_{24}]^{15}/[C_{12}H_{18}]^{20} = K_1\\
&[C_{20}H_{30}]^{12}/[C_{12}H_{18}]^{20} = K_2\\
&[C_{24}H_{36}]^{10}/[C_{12}H_{18}]^{20} = K_3\\
&[C_{20}H_{30}]^{12}/[C_{16}H_{24}]^{15} = K_4\\
&[C_{24}H_{36}]^{10}/[C_{16}H_{24}]^{15} = K_5\\
&[C_{24}H_{36}]^{10}/[C_{20}H_{30}]^{12} = K_6\\
&[C_{12}H_{18}] + [C_{16}H_{24}] + [C_{20}H_{30}] + [C_{24}H_{36}] = 1
\end{aligned} \tag{3}$$

where K are the respective equilibrium constants.

Results and Discussion

It has been reported that the metathesis degradation of polyalkenamers in dilute solution leads to a variety of cyclic oligomers and the chain-ring equilibrium is completely shifted towards the oligomeric rings.[1–4] Figure 2 presents the ring equilibrium for the intramolecular degradation of NR.

Table 1 shows the calculated thermodynamic parameters of cyclic oligomers for the intramolecular degradation of NR and *cis*-PB. As seen for the cyclic isoprene trimers the formation of the all-*trans* isomer becomes more preferable. Table 2 presents the calculated steric

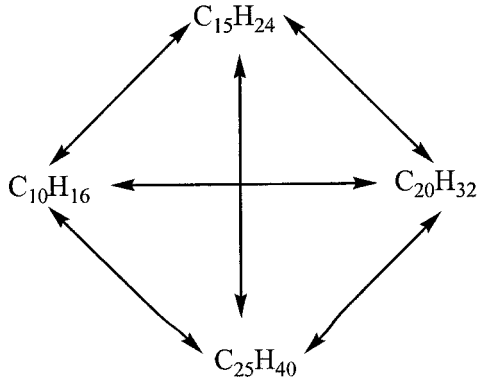

Figure 2. Equilibrium between cyclic isoprene oligomers.

Table 1. Calculated Gibbs free energy (G), enthalpy (H) and entropy (S) of cyclic oligomers for the intramolecular degradation of NR and *cis*-PB.

Compound	Formula	G	H	S
		kcal · mol^{-1}		cal · mol^{-1} · K
cc-CID[a]	$C_{10}H_{16}$	−243309.8	−243281.2	95.8
ccc-CIT[b]	$C_{15}H_{24}$	−364959.3	−364922.2	124.3
cct-CIT	$C_{15}H_{24}$	−364963.4	−364926.3	124.3
ctt-CIT	$C_{15}H_{24}$	−364963.9	−364927.0	123.9
ttt-CIT	$C_{15}H_{24}$	−364966.4	−364929.1	125.1
cccc-CITe[c]	$C_{20}H_{32}$	−486621.5	−486573.9	156.0
tttt-CITe	$C_{20}H_{32}$	−486619.7	−486572.6	158.1
ccccc-CIPe[d]	$C_{25}H_{40}$	−608267.7	−608213.8	180.7
ttttt-CIPe	$C_{25}H_{40}$	−608269.7	−608214.1	186.5
cc-CBD[e]	C_8H_{12}	−194350.9	−194325.9	83.4
ttt-CBT[f]	$C_{12}H_{18}$	−291537.6	−291506.7	103.6
tttt-CBTe[g]	$C_{16}H_{24}$	−388710.4	−388672.3	127.9
ttttt-CBPe[h]	$C_{20}H_{30}$	−485891.0	−485845.9	151.2
tttttt-CBHe[i]	$C_{24}H_{36}$	−583068.3	−583015.6	176.8

[a, b, c, d] Cyclic oligomers containing 2, 3, 4, 5 isoprene units, respectively.
[e, f, g, h, i] Cyclic oligomers containing 2, 3, 4, 5, 6 butadiene units, respectively.

Table 2. MM2 steric energies of cyclic isoprene tetramers ($C_{20}H_{32}$) and pentamers ($C_{25}H_{40}$).

Isomer distribution for $C_{20}H_{32}$	E_{min} [a] kcal · mol^{-1}	Isomer distribution for $C_{25}H_{40}$	E_{min} [a] kcal · mol^{-1}
cccc	19.6	*ccccc*	22.6
tccc	20.2	*tcccc*	22.2
ttcc	19.8	*ttccc*	22.2
tttc	21.5	*tttcc*	23.1
tttt	20.1	*ttttc*	24.1
		ttttt	23.9

[a] E_{min} = steric energy as stated in MM2 model.

energy for the cyclic isoprene tetramers and pentamers at MM2 level. It is seen that the formation of the all-*cis* cyclic tetramer and pentamer is slightly more preferable than the formation of the all-*trans* isomer. The steric energy term is smaller in the *cis*-isomer due to the weaker interactions between methyl substituents. Figure 3 shows the structures of the lowest energy conformers of cyclic isoprene tetramers optimized by MM2 force field**.**

It is important to note that for cyclic butadiene oligomers the decrease in the steric energy occurs from the all-*cis* to the all-*trans* isomers and the difference in steric and the free Gibbs energies between these isomers is about 5–6 kcal/mol.[17] The obtained results suggested that the intramolecular degradation of NR, in contrast to *cis*-PB, will result in the formation of *cis*-containing rings (except for cyclic isoprene trimers). These results are in good agreement with experimental data. It has been reported that the metathesis degradation of *cis*-PI by W-

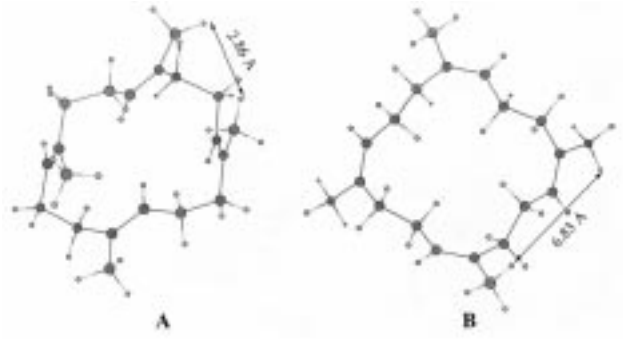

Figure 3. Lowest energy conformers located for all-*trans* (A) and all-*cis* (B) cyclic isoprene tetramer ($C_{20}H_{32}$) using simulate annealing technique.

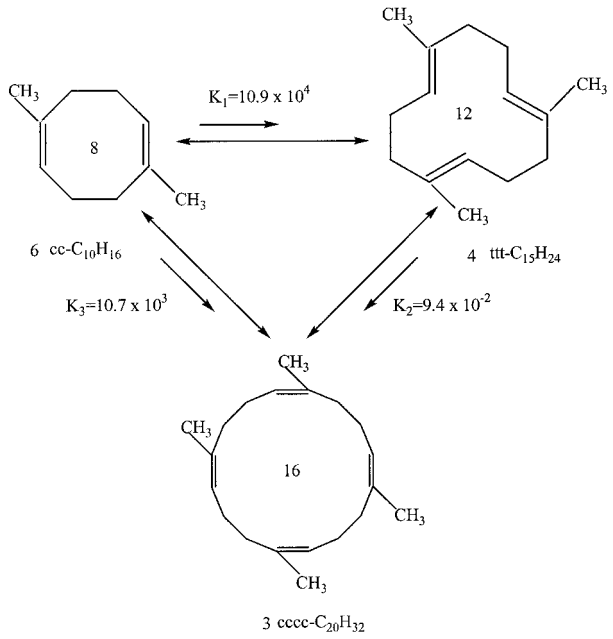

Figure 4. Ring-ring equilibrium between *cc*-$C_{10}H_{16}$, *ttt*-$C_{15}H_{24}$ and *cccc*-$C_{20}H_{32}$.

containing catalyst is not accompanied by *cis-trans* isomerization, while *cis*-PB under the same conditions degrades to cyclic oligomers with predominant *trans*-configuration of double bonds.[2, 8, 16] Table 3 presents the theoretical values of ΔG, ΔH and ΔS for the simple isoprene ring-ring equilibrium. It is seen that from all rings the formation of the cyclic oligomers containing *trans* isoprene trimer and *cis* tetramer is thermodynamically favored. In the Table 4 the calculated ΔG and equilibrium constant (K) for the cyclic isoprene and butadiene oligomers are listed. Table 4 shows that the ring-ring equilibrium for the isoprene oligomers is shifted towards the *ttt*-$C_{15}H_{24}$ and *cccc*-$C_{20}H_{32}$. Figure 4 illustrates the equilibrium between *cis-cis* cyclic isoprene dimer, all-*trans* trimer and all-*cis* tetramer. As seen from Figure 4 the formation of the all-*trans* cyclic isoprene trimers is thermodynami-

Table 3. Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) differences for the cyclic isoprene oligomers equilibrium at 298.15 K.

Ring-ring equilibrium	ΔG	ΔH	ΔS
	kcal · mol^{-1}		cal · mol^{-1} · K^{-1}
3 *cc*-$C_{10}H_{16}$ ⇌ 2 *ccc*-$C_{15}H_{24}$	10.8	–0.8	–38.9
3 *cc*-$C_{10}H_{16}$ ⇌ 2 *cct*-$C_{15}H_{24}$	2.7	–9.3	–39.0
3 *cc*-$C_{10}H_{16}$ ⇌ 2 *ctt*-$C_{15}H_{24}$	1.5	–10.3	–39.7
3 *cc*-$C_{10}H_{16}$ ⇌ 2 *ttt*-$C_{15}H_{24}$	–3.4	–14.6	–37.3
2 *cc*-$C_{10}H_{16}$ ⇌ *cccc*-$C_{20}H_{32}$	–1.8	–11.5	–35.7
2 *cc*-$C_{10}H_{16}$ ⇌ *tttt*-$C_{20}H_{32}$	–0.8	–10.1	–33.6
5 *cc*-$C_{10}H_{16}$ ⇌ 2 *ccccc*-$C_{25}H_{40}$	13.8	–21.4	–117.9
5 *cc*-$C_{10}H_{16}$ ⇌ 2 *ttttt*-$C_{25}H_{40}$	9.7	–21.9	–106.2
4 *ttt*-$C_{15}H_{24}$ ⇌ 3 *cccc*-$C_{20}H_{32}$	1.4	–5.3	–32.3
4 *ttt*-$C_{15}H_{24}$ ⇌ 3 *tttt*-$C_{20}H_{32}$	6.6	–1.1	–26.0
ccc-$C_{15}H_{24}$ ⇌ *ttt*-$C_{15}H_{24}$	–6.7	–6.9	0.8
cccc-$C_{20}H_{32}$ ⇌ *tttt*-$C_{20}H_{32}$	2.7	1.4	2.1
ccccc-$C_{25}H_{40}$ ⇌ *ttttt*-$C_{25}H_{40}$	–2.0	–0.3	5.8
5 *ttt*-$C_{15}H_{24}$ ⇌ 3 *ttttt*-$C_{25}H_{40}$	23.2	3.6	–66.3
5 *cccc*-$C_{20}H_{32}$ ⇌ 4 *ccccc*-$C_{25}H_{40}$	36.7	14.6	–57.3
5 *tttt*-$C_{20}H_{32}$ ⇌ 4 *ttttt*-$C_{25}H_{40}$	19.9	6.6	–44.7

Table 4. Calculated ΔG and equilibrium constant (K) for the cyclic isoprene and butadiene oligomers at 298.15 K.

Reaction	ΔG	K
	kcal · mol^{-1}	
5 *cc*-$C_{10}H_{16}$ ⟺ 2 *ttt*-$C_{15}H_{24}$ + *cccc*-$C_{20}H_{32}$	–5.3	$7.24 \cdot 10^{3}$
3 *ttt*-$C_{15}H_{24}$ ⟺ *cccc*-$C_{20}H_{32}$ + *ccccc*-$C_{25}H_{40}$	10.2	$3.2 \cdot 10^{-8}$
cc-$C_{10}H_{16}$ + *cct*-$C_{15}H_{24}$ ⟺ *ccccc*-$C_{25}H_{40}$	5.6	$8.62 \cdot 10^{-5}$
3 *ttt*-$C_{15}H_{24}$ ⟺ *tttt*-$C_{20}H_{32}$ + *ttttt*-$C_{25}H_{40}$	9.9	$4.3 \cdot 10^{-8}$
2 *cct*-$C_{15}H_{24}$ + *cccc*-$C_{20}H_{32}$ ⟺ 2 *ccccc*-$C_{25}H_{40}$	12.9	$3.4 \cdot 10^{-10}$
2 *ttt*-$C_{15}H_{24}$ + *cccc*-$C_{20}H_{32}$ ⟺ 2 *ccccc*-$C_{25}H_{40}$	19.0	$1.1 \cdot 10^{-14}$
cccc-$C_{20}H_{32}$ + *ccccc*-$C_{25}H_{40}$ ⟺ *tttt*-$C_{20}H_{32}$ + *ttttt*-$C_{25}H_{40}$	–0.3	1.54
9 *cc*-$C_{8}H_{12}$ ⟺ *ttt*-$C_{12}H_{18}$ + *tttt*-$C_{16}H_{24}$ + *ttttt*-$C_{20}H_{30}$ + *tttttt*-$C_{24}H_{36}$	–49.8	$3.3 \cdot 10^{36}$
5 *ttt*-$C_{12}H_{18}$ ⟺ *tttt*-$C_{16}H_{24}$ + *ttttt*-$C_{20}H_{30}$ + *tttttt*-$C_{24}H_{36}$	18.3	$4.1 \cdot 10^{-14}$

Table 5. Calculated and experimentally observed ring distributions for the intramolecular degradation of NR and *cis*-PB at 298.15 K.

Cyclic isoprene oligomers	Calculated mole fraction of oligomers in %	Cyclic butadiene oligomers	Mole fraction of oligomers in %[9, 21]	Calculated mole fraction of oligomers in %
cc-$C_{10}H_{16}$	11	$C_{12}H_{18}$	81.4	99.8
ttt-$C_{15}H_{24}$	64	$C_{16}H_{24}$	5.4	<0.1
cccc-$C_{20}H_{32}$	25	$C_{20}H_{30}$	6.3	0.1
		$C_{24}H_{36}$	4.0	<0.1
		$C_{28}H_{42}$	2.0	

cally preferred. The equilibrium distribution between these cyclic oligomers is presented in Table 4.

According to the calculations, the main product of the intramolecular metathesis degradation of NR at 298.15 K is the *trans-trans-trans* cyclic isoprene trimer (64 mol-%). It is important to note that cyclobutene ring is not formed because of the ring strain[20] while the formation of the cyclic isoprene dimers from larger rings is thermodynamically favored. On the other hand, the formed *cis*,*cis*-1,5-dimethyl-1,5-cyclooctadiene can participate in the metathesis oligomerization to form the *trans* cyclic isoprene trimer and the *cis* cyclic tetramer (Table 4). It means that the ring-opening metathesis polymerization (ROMP) of *cis*,-*cis*-1,5-dimethyl-1,5-cyclooctadiene in dilute solution (below the critical concentration) at equilibrium will give cyclic isoprene trimer and tetramer similar to these from the intramolecular metathesis degradation of NR (cf. Table 5). The cyclooligomerization of *cis*,*cis*-1,5-dimethyl-1,5-cyclooctadiene to *trans*,*trans,trans*-1,5,9-trimethyl-1,5,9-cyclododecatriene is depicted in Figure 5. In

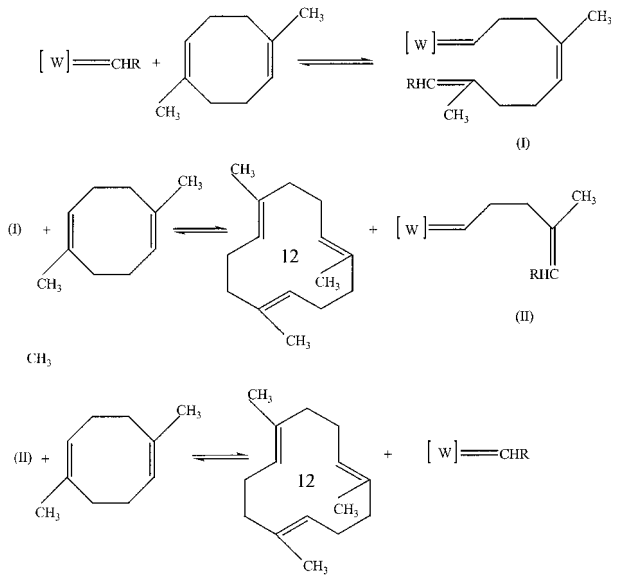

Figure 5. Cyclooligomerization of *cis*,*cis*-1,5-dimethyl-1,5-cyclooctadiene to *trans*,*trans*,*trans*-1,5,9-trimethyl-1,5,9-cyclododecatriene.

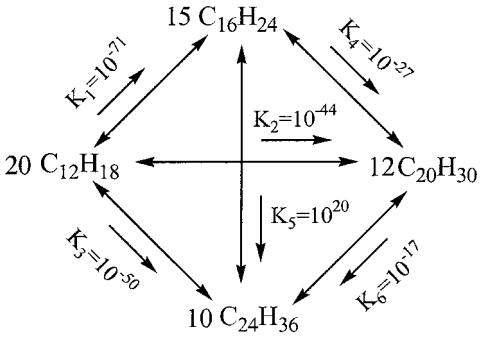

Figure 6. Equilibrium between all-*trans* cyclic oligomers for the intramolecular degradation of *cis*-PB.

contrast to *cis*,*cis*-1,5-dimethyl-1,5-cyclooctadiene, *cis*,-*cis*-1,5-cyclooctadiene easily participates in the ring-opening metathesis oligomerization producing all-*trans* oligomers.

Figure 6 shows the equilibrium between these cyclooligomers. As seen the equilibrium is completely shifted towards the all-*trans* cyclic trimer. Table 4 presents the experimentally observed and calculated distributions of the all-*trans* cyclic butadiene oligomers. These results are in reasonable agreement with recent experimental data.[9, 21]

The calculations show that NR in the presence of appropriate high stable catalysts can degrade to a set of *cis* cyclic oligomers which undergo the further metathesis degradation to the thermodynamically more stable rings with the all-*trans* cyclic isoprene trimers being the main products (Figure 7). It is well known that if the formation of a certain cycle becomes thermodynamically favored,

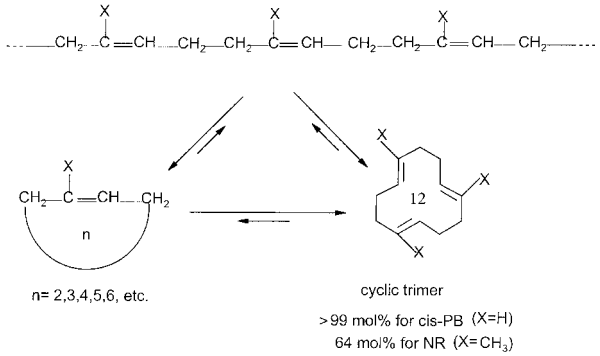

Figure 7. Equilibrium for the intramolecular metathesis degradation of *cis*-PB and NR.

the intramolecular metathesis degradation of polyalkenamers can be shifted completely towards these rings. Thus, it has been shown that the intramolecular metathesis degradation of the alternating copolymer of butadiene and propylene at room temperature proceeded at first stage to yield small amounts of the 4-methyl-1-cyclohexene and cyclic oligomers with the general formula $(C_7H_{12})_n$, where $n = 3–7$. At the final stage these large rings are completely degraded to the thermodynamically more stable 4-methyl-1-cyclohexene.[2]

Conclusions

The calculations show that the main product of the intramolecular metathesis degradation of NR is *trans*-*trans*-*trans*-1,5,9-trimethyl-1,5,9-cyclododecatriene. It follows that the ROMP of *cis*,*cis*-1,5-dimethyl-1,5-cyclooctadiene in dilute solution will produce mainly all-*trans* cyclic isoprene trimer similar to that of the intramolecular metathesis degradation of NR. As seen from the calculations NR in a dilute solution and by high active and long-time stable metathesis catalysts will degrade into a set of cyclic oligomers which undergo the further metathesis cyclodegradation to the thermodynamically more stable rings with the all-*trans* cyclic isoprene trimers being the main products. The steric energies obtained from the MM2 model are very similar for *cis*, *cis*-*trans* and *trans* isomers (except for the cyclic trimers). Hence, it is not surprising that the degradation of NR by metathesis catalysts will give at the first stage *cis* cyclic oligomers which are transformed to the thermodynamically more stable *trans* cyclic isoprene trimer.

According to the HF/6–31G* model the ring-ring equilibrium for the intramolecular degradation of *cis*-PB is completely shifted towards the all-*trans* cyclic trimer. These results are in reasonably agreement with recently obtained experimental data.

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