

Density functional theory study of ring-chain equilibria for the cross-metathesis of cyclohexene and *cis,cis*-cycloocta-1,5-diene with functionalized olefins

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Abstract

The computational modeling of ring-chain equilibria for the ring-opening cross-metathesis of cyclohexene (CH) with 1,2-dicarbomethoxy-ethylene (DCE), 1,4-dicarbomethoxy-but-2-ene (DCB) and ethylene at $T = 298.15$ K using the B3LYP/6-31G(d,p) level of theory revealed that CH and ring-opened products equilibrium is shifted towards the thermodynamically stable six-membered ring. The calculations demonstrated that carbonyl-containing olefins can completely drive the equilibrium in the cross-metathesis with *cis,cis*-cycloocta-1,5-diene (COD) towards the ring-opened products.

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1. Introduction

Ring-opening metathesis polymerization (ROMP) of many cyclic olefins is thermodynamically controlled reaction and thermodynamic data can be used for the prediction of cyclic olefins polymerizability *via* ring-opening metathesis. Taking into account that the ROMP is an equilibrium process, the estimated thermodynamic parameters of the reaction can predict the equilibrium products distributions in the system [1]. ROMP of three-, four-, eight-, and larger-membered cyclic olefins is thermodynamically favored and proceeds to form high molar mass polyalkenamers [1]. On the other hand, the six-membered rings do not undergo ROMP due to their low strain energy [1]. Such unreactive to ROMP rings can be prepared *via* ring-closing metathesis (RCM) of appropriate compounds. Thus, non-polymer-

izable *via* ROMP 4-methyl-cyclohexene has been prepared by RCM degradation of highly alternative butadiene-propylene copolymer [1,2]. It is worth noting that the sign of free energy difference (ΔG) for the ring-chain equilibrium process may be sensitive to a number of factors, such as monomer concentration, temperature, nature of substituents in the ring, etc. There is some evidence of cyclohexene (CH) polymerizability *via* metathesis to yield a small proportion of oligomers at low temperature and high monomer concentration [1]. It was recently shown [3] that thermodynamically stable CH can be ring-opened *via* metathesis in the presence of α -carbonyl-containing olefins as chain transfer agents (CTAs) using the ruthenium alkylidene catalysts. The development of new generation highly active metal-alkylidene catalysts opens new possibilities in olefin metathesis and its application to well-defined products synthesis [4–6]. These catalysts display a broad functional group tolerance and make it possible to metathesize sterically hindered and high functionalized olefins

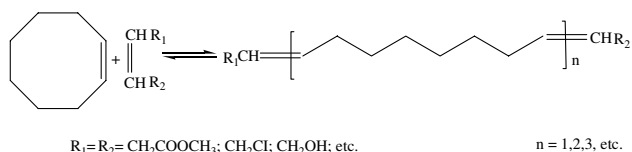
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[7]. In general, the new generation of metal–alkylidene complexes leads to the equilibrium between all species formed during the exchange of double bonds in the metathesis. Thus, thermodynamic data can be used for the calculation and prediction of products distributions in the olefin metathesis. The equilibrium distribution of the alkylidene species has been calculated for the metathesis of simple linear olefins [8]. The theoretical estimations of ring-chain products distributions for ROMP of cycloolefins have been published. [9]. We have studied the distributions of cyclic and linear products for the ring-opening cross-metathesis of *cis,cis*-cycloocta-1,5-diene (COD) and *cis,cis*-1,5-dimethyl-cycloocta-1,5-diene with ethylene (ethenolysis) using the ab initio approach [10–12]. ROMP of cycloolefins in the presence of functionalized olefins as CTAs yields end-functionalized polymers (telechelics) (scheme 1). The telechelics are very useful as cross-linking agents and intermediates in the synthesis of block copolymers and polymeric networks [13]. Ring-opening cross-metathesis of cycloolefins with ethylene leads to α,ω -diolefins which can be used as starting compounds in the production of fine chemicals [1,14].

The goal of this paper is density functional theory calculations of ring-chain equilibria for the ring-opening cross-metathesis of CH and COD with α - and β -carbonyl-containing olefins at $T = 298.15$ K.

2. Computational details

All geometry optimizations were run using the Gaussian-98 [15] revision A9 package without any symmetry restriction. Lowest energy conformers were located using a Monte-Carlo algorithm as implemented in the Titan package version 1.0.5. [16]. Lowest energy conformers found were used as initial structures for the geometry optimization using Becke's parameter functional (*B*) [17] in combination with the Lee, Yang and Parr (LYP) correlation function [18] and the 6-31G(d,p) standard basis set. The molecular geometries of the all calculated molecules were optimized to a global minimum at B3LYP/6-31G(d,p) level of theory followed by frequency calculations at $T = 298.15$ 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



Scheme 1. Synthesis of telechelics *via* ring-opening cross-metathesis.

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

where R is the universal gas constant, T is the absolute temperature and ΔG is the standard free energy reaction difference. The equilibrium concentrations of *cis*- and *trans*- $C_6H_8O_4$, C_6H_{10} , *trans,trans,trans*- $C_{14}H_{22}O_4$, *cis,cis*- C_8H_{12} , *trans*- $C_{10}H_{14}O_4$, *trans*- $C_{10}H_{16}$, hexa-1,5-diene (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):

$$\begin{aligned} [ttt-C_{14}H_{20}O_4]/([cc-C_8H_{12}][c-C_6H_8O_4]) &= K_1, \\ [ttt-C_{14}H_{20}O_4]/([cc-C_8H_{12}][t-C_6H_8O_4]) &= K_2, \\ [ttt-C_{14}H_{20}O_4] + [cc-C_8H_{12}] + [C_6H_8O_4] &= 1, \\ [tt-C_{10}H_{14}O_4]^4/([ttt-C_{14}H_{20}O_4][cc-C_8H_{12}][t-C_6H_8O_4]^3) &= K_3, \\ [tt-C_{10}H_{14}O_4] + [ttt-C_{14}H_{20}O_4] + [cc-C_8H_{12}] + [t-C_6H_8O_4] &= 1, \\ [C_6H_{10}]^4/([cc-C_8H_{12}][t-C_{10}H_{16}][C_2H_4]^3) &= K_4, \\ [C_6H_{10}] + [cc-C_8H_{12}] + [t-C_{10}H_{16}] + [C_2H_4] &= 1, \end{aligned} \quad (2)$$

where K_1 – K_4 are respective equilibrium constants.

3. Results

Table 1 shows the calculated thermodynamic parameters of cyclic and linear molecules for the cross-metathesis of CH and COD with DCE, DCB and ethylene at $T = 298.15$ K. The thermodynamic parameters have been calculated only for the all *trans*-isomer products. It has been shown that the formation of *trans*-isomers is more preferable compared to *cis*-compounds [11]. Table 2 presents the calculated standard free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) differences of ring-linear molecules equilibrium for the ring-opening cross-metathesis of CH and COD with olefins at $T = 298.15$ K. It is seen that CH can open *via* cross-metathesis with thermodynamically highly unstable *cis*-DCE to yield the ring-opened *trans-trans*-1,8-dicarbomethoxy-octa-1,7-diene (scheme 2). Figure 1 shows the calculated minimum energy conformer of *trans-trans*-1,8-dicarbomethoxy-octa-1,7-diene. The standard free energy values (ΔG) for the cross-metathesis of CH with *cis*- and *trans*-DCE are -9.5 and $18 \text{ kJ} \cdot \text{mol}^{-1}$, respectively (table 2, entries 1 and 2, scheme 2). The calculations show that *cis*-DCE is thermodynamically more unstable compared to *trans*-DCE and the difference the standard free energies between *cis*- and *trans*-isomers is about $26 \text{ kJ} \cdot \text{mol}^{-1}$ (table 1). It means that thermodynamically unstable *cis*-DCE will easily isomerize to *trans*-isomer during the metathesis shifting the equilibrium towards the CH. Molecular modeling reveals that the low stereoselectivity for the metathesis reaction is due to the close matching of activation energies for the *cis* and *trans* isomer formation and the fast *cis-trans*

TABLE 1

Calculated standard free energy (G°), enthalpy (H°) and entropy (S°) of cyclic and linear molecules for the ring-opening cross-metathesis of cyclohexene (CH) and *cis,cis*-cycloocta-1,5-diene (COD) with 1,4-dicarbomethoxy-but-2-ene (DCB), 1,2-dicarbomethoxy-ethylene (DCE) and ethylene at $T = 298.15$ K

Compound	Formula	$10^{-5} G^\circ / (\text{kJ} \cdot \text{mol}^{-1})$	$10^{-5} H^\circ / (\text{kJ} \cdot \text{mol}^{-1})$	$S^\circ / (\text{kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
COD	C_8H_{12}	-8.19478	-8.19790	351.7
CH	C_6H_{10}	-6.16239	-6.16147	309.4
<i>tt</i> -1,10-DCD ^a	$\text{C}_{14}\text{H}_{22}\text{O}_4$	-22.26352	-22.26141	706.2
<i>tt</i> -1,8-DCO ^b	$\text{C}_{12}\text{H}_{18}\text{O}_4$	-20.19917	-20.19729	631.8
<i>ttt</i> -1,10-DCMD ^c	$\text{C}_{14}\text{H}_{20}\text{O}_4$	-22.22117	-22.21929	629.8
<i>tt</i> -1,6-DCMH ^d	$\text{C}_{10}\text{H}_{14}\text{O}_4$	-18.12583	-18.12417	557.4
<i>tt</i> -deca-1,5,9-triene	$\text{C}_{10}\text{H}_{16}$	-10.25903	-10.25030	465.6
<i>tt</i> -deca-2,8-diene	$\text{C}_{10}\text{H}_{18}$	-10.29117	-10.28974	479.4
octa-1,7-diene	C_8H_{14}	-8.22625	-8.22502	414.3
<i>c</i> -DCB	$\text{C}_8\text{H}_{12}\text{O}_4$	-16.10149	-16.09990	533.0
<i>c</i> -DCE	$\text{C}_6\text{H}_8\text{O}_4$	-14.03669	-14.03537	442.6
<i>t</i> -DCE	$\text{C}_6\text{H}_8\text{O}_4$	-14.03696	-14.03564	441.7
hexa-1,5-diene	C_6H_{10}	-6.16162	-6.16058	406.2
<i>c</i> -but-2-ene	C_4H_6	-4.12909	-4.12819	301.5
<i>t</i> -but-2-ene	C_4H_6	-4.12914	-4.12825	297.7
Ethylene	C_2H_4	-2.06418	-2.06351	224.8

^a *tt*-1,10-DCD – *tt*-1,10-dicarbomethoxy-deca-2,8-diene.

^b *tt*-1,8-DCO – *tt*-1,8-dicarbomethoxy-octa-1,7-diene.

^c *ttt*-1,10-DCMD – *ttt*-1,10-dicarbomethoxy-deca-1,5,9-triene.

^d *tt*-1,6-DCMH – *tt*-1,6-dicarbomethoxy-hexa-1,5-diene.

TABLE 2

Standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) differences of ring-chain equilibria for the ring-opening cross-metathesis of CH and COD with DCB, DCE and ethylene at $T = 298.15$ K

Entry	Reaction	$\Delta G^\circ \text{ kJ} \cdot \text{mol}^{-1}$	$\Delta H^\circ \text{ kJ} \cdot \text{mol}^{-1}$	$\Delta S^\circ \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}$
1	$\text{C}_6\text{H}_{10} + c\text{-C}_6\text{H}_8\text{O}_4 \leftrightarrow tt\text{-C}_{12}\text{H}_{18}\text{O}_4^a$	-9.5	-45.0	-120.2
2	$\text{C}_6\text{H}_{10} + t\text{-C}_6\text{H}_8\text{O}_4 \leftrightarrow tt\text{-C}_{12}\text{H}_{18}\text{O}_4^a$	18.0	-18.0	-119.3
3	$\text{C}_6\text{H}_{10} + c\text{-C}_8\text{H}_{12}\text{O}_4 \leftrightarrow tt\text{-C}_{14}\text{H}_{22}\text{O}_4^b$	36.4	-4.3	-136.2
4	$\text{C}_6\text{H}_{10} + c\text{-C}_4\text{H}_6 \leftrightarrow tt\text{-C}_{10}\text{H}_{16}^c$	31.0	-8.0	-131.5
5	$\text{C}_6\text{H}_{10} + \text{C}_2\text{H}_4 \leftrightarrow \text{C}_8\text{H}_{14}^c$	32.0	-4.0	-119.9
6	$\text{C}_8\text{H}_{12} + t\text{-C}_6\text{H}_8\text{O}_4 \leftrightarrow ttt\text{-C}_{14}\text{H}_{20}\text{O}_4^d$	-5.5	-54.1	-163.2
7	$\text{C}_8\text{H}_{12} + ttt\text{-C}_{14}\text{H}_{20}\text{O}_4 + 3t\text{-C}_6\text{H}_8\text{O}_4 \leftrightarrow 4\text{-}tt\text{-C}_{10}\text{H}_{14}\text{O}_4^e$	-54.7	-77.5	-76.2
8	$\text{C}_8\text{H}_{12} + t\text{-C}_{10}\text{H}_{16} + 3\text{C}_2\text{H}_4 \leftrightarrow 4\text{C}_6\text{H}_{10}^f$	-13.0	-41.9	-94.9

^a Scheme 1.

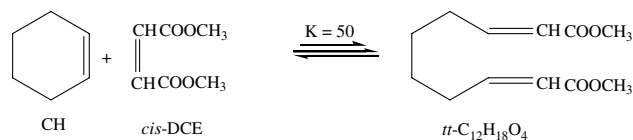
^b Scheme 2.

^c Scheme 3.

^d Scheme 4.

^e Scheme 5.

^f Scheme 6.



Scheme 2. Ring-opening cross-metathesis of CH with DCE to *trans,trans*-1,8-dicarbomethoxy-octa-1,7-diene.

isomerization by catalyst leading to an equilibrium mixture of the isomers [19]. Interestingly, β -functionalized olefin DCB behaved quite differently from α -functionalized DCE. The value of standard free energy for the ring-opening cross-metathesis of CH with β -functional-

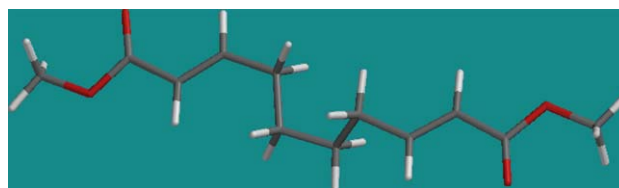
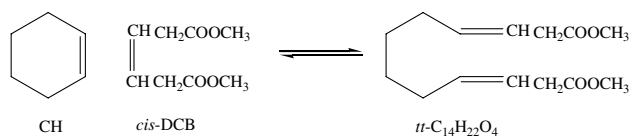
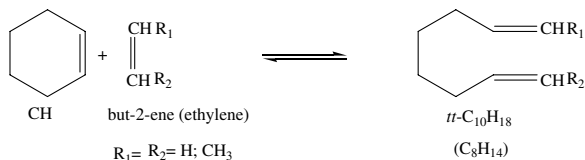


FIGURE 1. Lowest energy conformer of *trans,trans*-1,8-dicarbomethoxy-octa-1,7-diene.

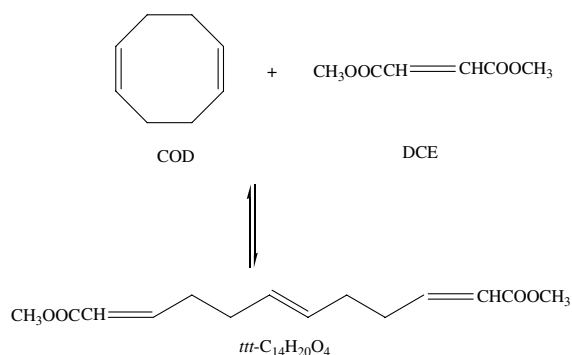
ized olefin to *tt*-1,10-dicarbomethoxy-deca-2,8-diene is $36.4 \text{ kJ} \cdot \text{mol}^{-1}$ (table 2, entry 3, scheme 3). Table 2 (entries 4 and 5, scheme 4) presents the calculated standard



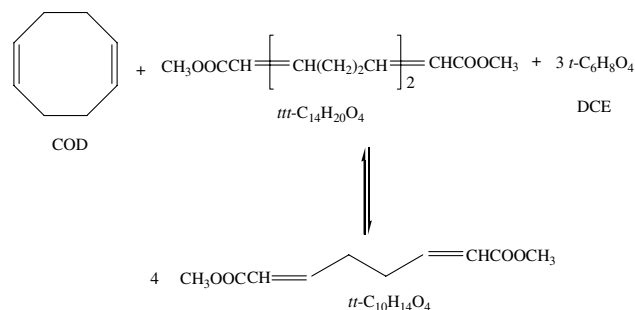
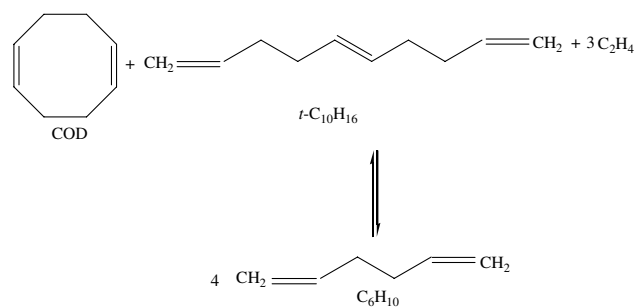
Scheme 3. Ring-opening cross-metathesis of CH with DCB.



Scheme 4. Ring-opening cross-metathesis of CH with but-2-ene and ethylene.

Scheme 5. Ring-opening cross-metathesis of COD with DCE to *trans,trans,trans*-1,10-dicarbomethoxy-deca-1,5,9-triene.

free energy differences for the ring-opening cross-metathesis of CH with but-2-ene and ethylene. As seen from table 2, ring-chain equilibria for the ring-opening cross-metathesis of COD with DCE is completely shifted to the formation of ring-opened products (entries 6 and 7, table 2, schemes 5 and 6). Table 2 (entry 8) also presents the thermodynamics for the ethenolysis of COD to hexa-1,5-diene (scheme 7). Table 3 summarizes the calculated standard free energies differences (ΔG) and equilibrium constants (K) for the ring-opening cross-metathesis of CH and COD with olefins at $T =$

Scheme 6. Ring-opening cross-metathesis of COD with DCE to *trans,trans*-1,6-dicarbomethoxy-hexa-1,5-diene.

Scheme 7. Ethenolysis of COD to hexa-1,5-diene.

298.15 K. As seen from table 3, ring-chain equilibrium for the cross-metathesis of COD with DCE is completely shifted towards the monomeric diene *trans-trans*-1,6-dicarbomethoxy-hexa-1,5-diene. The ring-chain equilibrium constants depend on the linear olefins used. Thus, the equilibrium constants for the COD and DCE cross-metathesis and ethenolysis of COD are $59 \cdot 10^8$ and 188, respectively (entries 5 and 6, table 3). Table 4 shows equilibrium distributions of molecules in the cross-metathesis of COD with DCE and ethylene. It is seen that ROMP of COD in the presence of DCE as a CTA (COD/DME = 1 or 2) proceeds with high selectivity to yield *trans,trans,trans*-1,10-dicarbomethoxy-deca-1,5,9-triene and monomeric *trans,trans*-1,6-dicarbomethoxy-hexa-1,5-diene. The concentration of hexa-1,5-diene at equilibrium with COD, *trans*-C₁₀H₁₆

TABLE 3

Standard free energy differences (ΔG°) and equilibrium constants (K) of ring-chain equilibria for the ring-opening cross-metathesis of CH and COD with DCE and ethylene at $T = 298.15$ K

Entry	Reaction	$\Delta G^\circ / (\text{kJ} \cdot \text{mol}^{-1})$	K
1	C ₆ H ₁₀ + <i>c</i> -C ₆ H ₈ O ₄ \rightleftharpoons <i>tt</i> -C ₁₂ H ₁₈ O ₄ ^a	-9.5	49
2	C ₆ H ₁₀ + <i>t</i> -C ₆ H ₈ O ₄ \rightleftharpoons <i>tt</i> -C ₁₂ H ₁₈ O ₄ ^a	18.0	9.5×10^{-4}
4	C ₈ H ₁₂ + <i>t</i> -C ₆ H ₈ O ₄ \rightleftharpoons <i>ttt</i> -C ₁₄ H ₂₀ O ₄ ^b	-5.5	10
5	C ₈ H ₁₂ + <i>ttt</i> -C ₁₄ H ₂₀ O ₄ + 3 <i>t</i> -C ₆ H ₈ O ₄ \rightleftharpoons 4 <i>tt</i> -C ₁₀ H ₁₄ O ₄ ^c	-54.7	59×10^8
6	C ₈ H ₁₂ + <i>t</i> -C ₁₀ H ₁₆ + 3C ₂ H ₄ \rightleftharpoons 4C ₆ H ₁₀ ^d	-13.0	188

^a Scheme 1.^b Scheme 4.^c Scheme 5.^d Scheme 6.

TABLE 4

Calculated cyclic and linear molecules distributions for the ring-opening cross-metathesis of COD with DCE and ethylene at $T = 298.15$ K

Reaction	Mole fraction in % of			
	C_8H_{12}	(A) C_2H_4	(B) $C_{10}H_{16}$	(C) $C_6H_{10}^a$
$C_8H_{12} + t-C_6H_8O_4$ (A) \rightleftharpoons $ttt-C_{14}H_{20}O_4$ (B)	13.5	13.5	73	
$C_8H_{12} + ttt-C_{14}H_{20}O_4 + 3t-C_6H_8O_4 \rightleftharpoons 4tt-C_{10}H_{14}O_4$ (C)	0.3	0.7		99
$C_8H_{12} + t-C_{10}H_{16} + 3C_2H_4 \rightleftharpoons 4C_6H_{10}^d$	10	10	31	49

^a The value of experimentally observed yield of hexa-1,5-diene (C_6H_{10}) for the ethenolysis of COD (ethylene/COD = 2) was 46 mol% [19].

^b Scheme 4.

^c Scheme 5.

^d Scheme 6.

and ethylene is 46 mol%. The calculations are in agreement with experimental data on the ethenolysis of COD by rhenium based catalysts [20]. It is worth noting that compared to monomeric *trans,trans*-1,6-dicarbomethoxy-hexa-1,5-diene, hexa-1,5-diene easily participated in acyclic diene metathesis oligomerization (ADMET) again producing *trans*-deca-1,5,9-triene ($t-C_{10}H_{16}$) (table 3, entries 5 and 6, schemes 5 and 6).

For the ring-chain equilibrium, the enthalpic change (ΔH) corresponds to the strain energy of ring, since the number and type of bonds are unchanged in the metathesis reaction. The reaction enthalpy in this case is a function of ring strain and *cis/trans* isomerization energy only. The calculated enthalpy change (ΔH) for the ring-opening cross-metathesis of cycloolefins with linear olefins will correspond to the strain energy of these monomers. Thus, the calculated value of ΔH for the cross-metathesis of CH with but-2-ene to *trans,trans*-deca-2,8-diene is $-8.0 \text{ kJ} \cdot \text{mol}^{-1}$. The experimentally obtained value of ΔH for conversion of CH into *trans*-ethylene-butadiene copolymer at $T = 298$ K is $-2.0 \text{ kJ} \cdot \text{mol}^{-1}$ [21]. It is seen that the agreement is reasonable. The calculated [11] and experimentally [22] obtained values of ΔH for conversion of COD into *trans*-polybutadiene at $T = 298$ K are -40.1 and $-33.0 \text{ kJ} \cdot \text{mol}^{-1}$, respectively.

References

- [1] K.J. Ivin, J.C. Mol, Olefin Metathesis and Metathesis Polymerization, Academic Press, San Diego, CA, 1997 (Chapters 8, 11 and 17).
- [2] Yu.V. Korshak, B.A. Dolgoplosk, M.A. Tlenkopatchev, Rec. Trav. Chim. Pays-Bas 96 (1977) M64–M67.
- [3] T.-L. Choi, Ch.W. Lee, A.K. Chatterjee, R.H. Grubbs, J. Am. Chem. Soc. 123 (2001) 10417–10418.
- [4] R.R. Schrock, Tetrahedron 55 (1999) 8141.
- [5] M.R. Buchmeiser, Chem. Rev. 100 (2000) 1565.
- [6] T.M. Trnka, R.H. Grubbs, Acc. Chem. Res. 34 (2001) 18.
- [7] C.W. Bielawski, R.H. Grubbs, Angew. Chem., Int. Ed. Engl. 39 (2000) 2903.
- [8] F. Kapteijn, E. Homburg, J.C. Mol, J. Chem. Thermodyn. 15 (1983) 147.
- [9] Z.-R. Chen, J.P. Claveria, R.H. Grubbs, J.A. Kornfield, Macromolecules 28 (1995) 2147–2154.
- [10] M.A. Tlenkopatchev, S.M. Vargas, S. Fomine, Tetrahedron 58 (2002) 4817–4824.
- [11] S. Gutierrez, S.M. Vargas, M.A. Tlenkopatchev, J. Chem. Thermodyn. 36 (2004) 29–36.
- [12] S. Gutierrez, S.M. Vargas, M.A. Tlenkopatchev, Polym. Degrad. Stab. 83 (2004) 149–156.
- [13] E.J. Goethals, Telechelic Polymers: Synthesis and Applications, CRC Press, Boca Raton, FL, 1989.
- [14] R.L. Banks, D.S. Banasiak, P.S. Hudson, R. Norell, J. Mol. Catal. 15 (1982) 21–26.
- [15] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98, Revision A.7, Gaussian, Inc., Pittsburgh, PA, 1998.
- [16] Titan 1.0.5 Version, Wavefunction Inc., Schrodinger Inc., 1999.
- [17] A.D. Becke, J. Chem. Phys. 98 (1993) 5648–5652.
- [18] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785–789.
- [19] M.A. Tlenkopatchev, S. Fomine, J. Organomet. Chem. 630 (2001) 157.
- [20] P. Chaumont, C.S. John, J. Mol. Catal. 46 (1988) 317–328.
- [21] B. Lebedev, N. Smirnova, T.G. Kulagina, Makromol. Chem., Rapid Commun. 9 (1988) 781–785.
- [22] B. Lebedev, N. Smirnova, Macromol. Chem. Phys. 195 (1994) 35–38.

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