Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Catalysis Science & Technology

Supporting Information

Depolymerization of 1,4-Polybutadiene by Metathesis: High Yield of Large Macrocyclic Oligo(butadiene)s by Ligand Selectivity Control

Annelies Dewaele,[a] Tom Renders,[a] Baoyi Yu,[b] Francis Verpoort,[b,c] Bert Sels[a,*]

[a] Center for Surface Science and Catalysis, KU Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium.

[b] Department of Inorganic and Physical Chemistry, Universiteit Gent, Krijgslaan 281, 9000 Gent, Belgium.

[c] Laboratory of Organometallics, Catalysis and Ordered Materials, State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China.

*E-mail: Bert.sels@biw.kuleuven.be

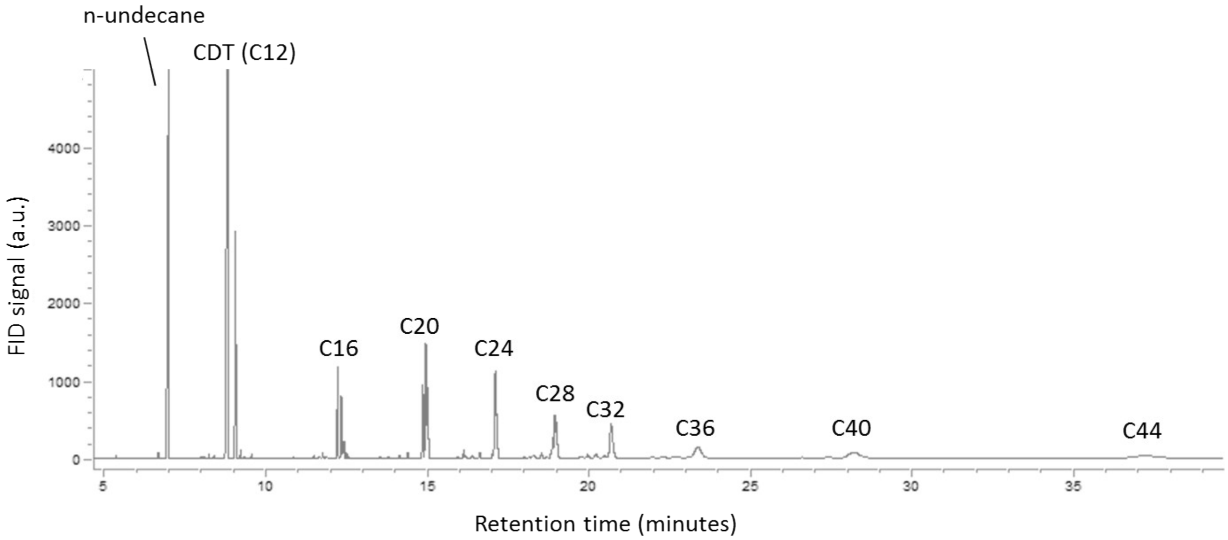

Figure S1. GC chromatogram after depolymerization of PB-250 000 with HG2 after 8h of reaction. Reaction conditions: 0.17 M -[C_4H_6]- (PB-250 000); 0.5 mol% Ru (HG2) ; 16 mL CH_2Cl_2 ; 308 K.

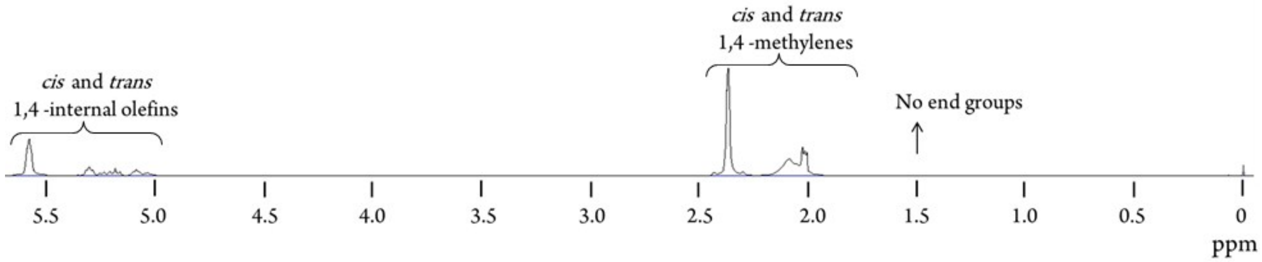

Figure S2. Olefin regions of a ^{1}H-NMR spectrum (300 MHz; $CDCl_3$) of a depolymerization reaction with PB-250 000. Tetramethylsilane (TMS) is the reference. Reaction conditions: 0.08 M -[C_4H_6]- (PB-250 000); 0.5 mol% Ru (HG2); 16 mL CH_2Cl_2 ; 308 K.

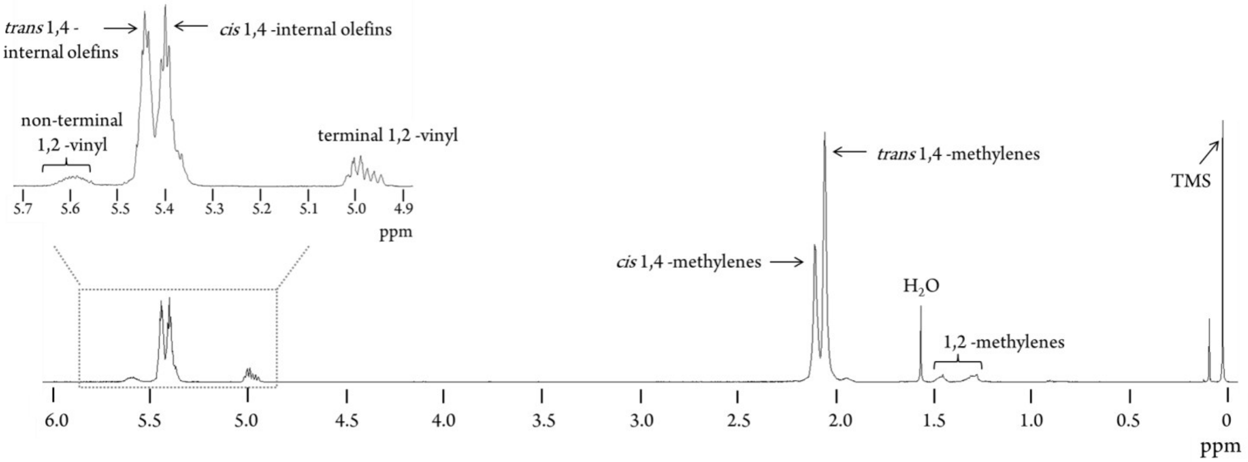

Figure S3. Olefin regions of a ^{1}H-NMR spectrum (300 MHz; $CDCl_3$) of polybutadiene. The resonance groups at 5.6, 5.45, 5.4, 5.0, 2.1 and 1.3-1.4 ppm represent non-terminal 1,2-vinyl olefins, *trans* 1,4-internal olefins, *cis* 1,4-internal olefins, terminal 1,2-vinyl olefins, 1,4-methylenes and 1,2-methylenes, respectively. Tetramethylsilane (TMS) is the reference.

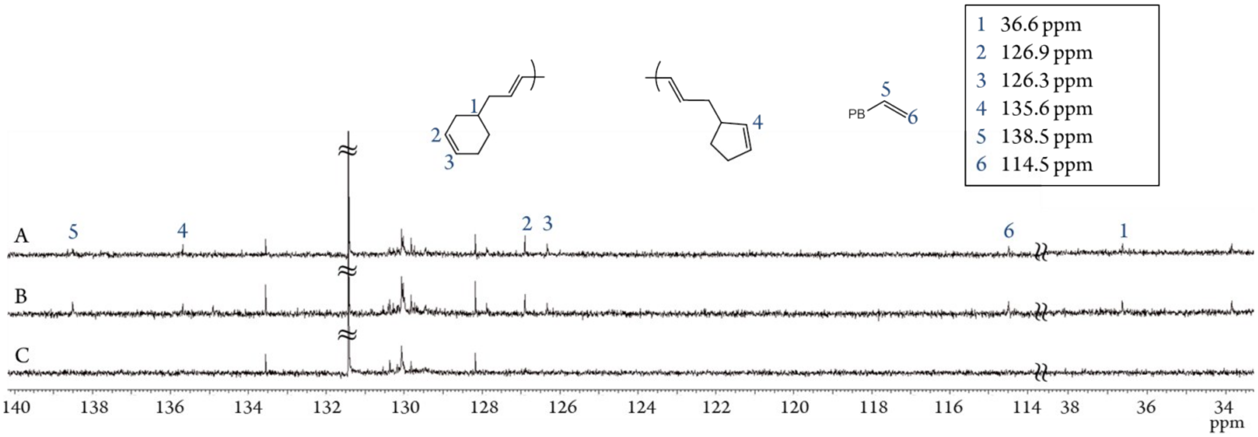

Figure S4. ^{13}C-NMR spectra (300 MHz, $CDCl_3$) after depolymerization of (A) PB-500 000 (10 % vinyl); (B) PB-200 000 (11 % vinyl) and (C) PB-250 000 (2 % vinyl). The characteristic resonance groups of cyclopentene, cyclohexene and vinyl-substituted PB are observed with vinyl-containing polybutadiene A and B, but not with polybutadiene C.

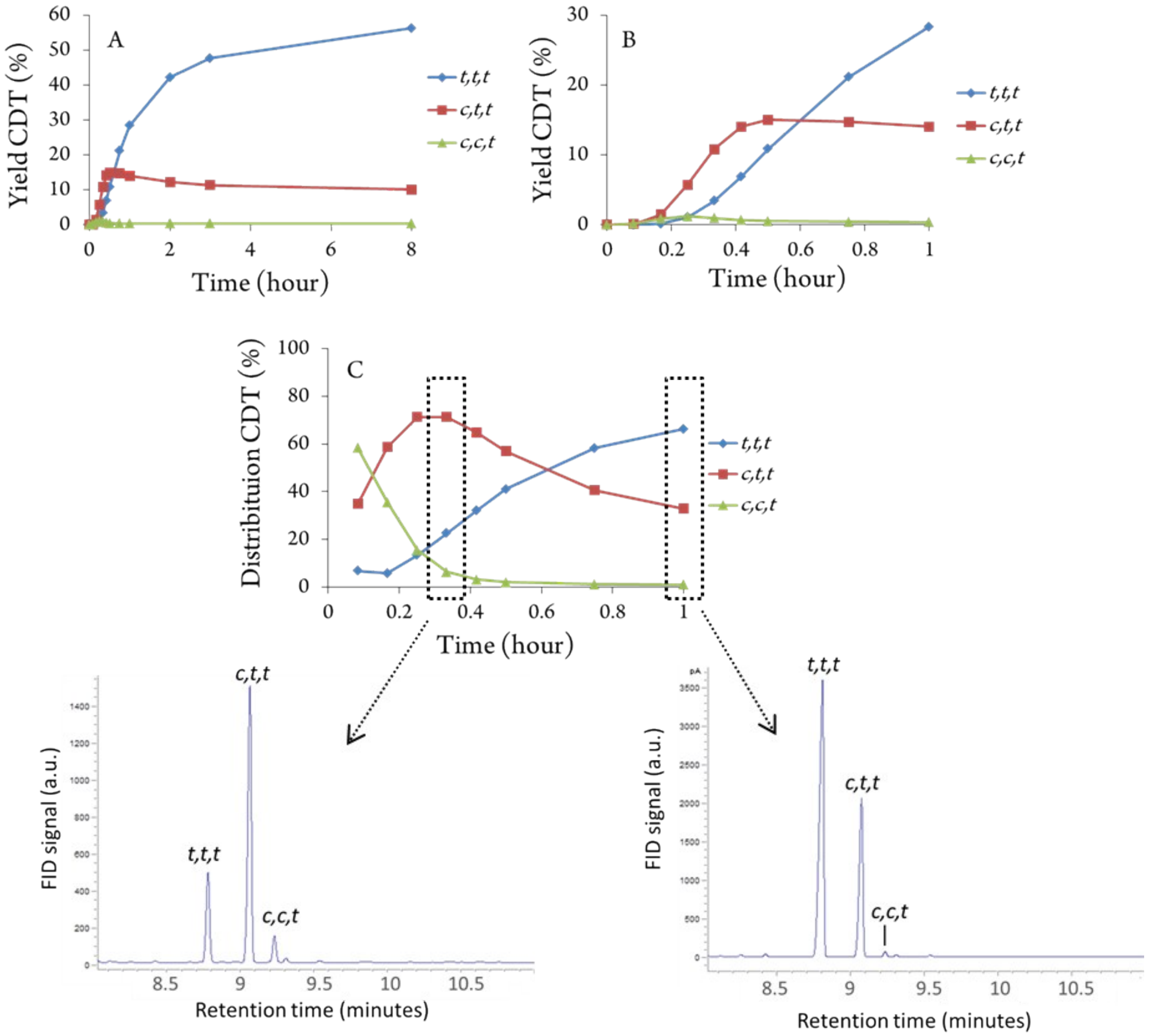

Figure S5. (A) Yield of CDT-isomers from PB-250 000 in time. (B) Yield of CDT-isomers from PB-250 000 during the first hour of reaction. (C) Distribution of CDT-isomers in time together with corresponding GC chromatograms after 30 min and 1h reaction time assigning the different CDT-isomers. Reaction conditions: 0.17 M -[C_4H_6]- (PB-250 000); 0.5 mol% Ru (HG2); 16 mL CH_2Cl_2 ; 308 K.

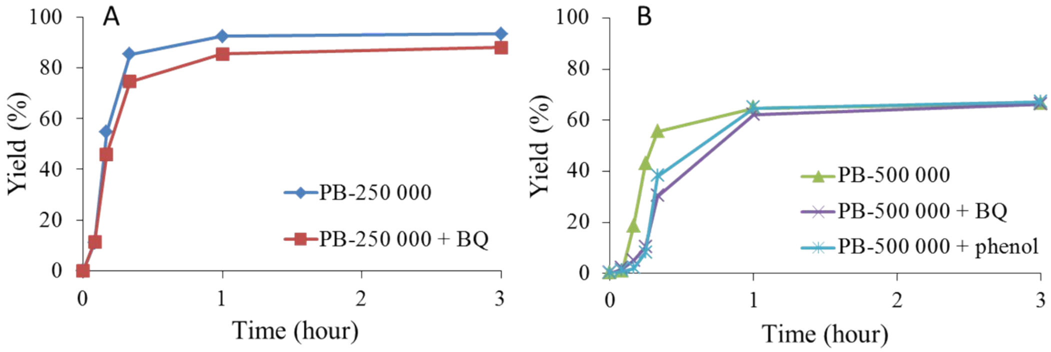

Figure S6. The effect of anti-isomerization additives on the yield of cyclic oligomers (C12-C44) in the depolymerization of (A) PB-250 000 and (B) PB-500 000. Reaction conditions: 0.17 M -[C_4H_6]- ; 0.5 mol% Ru (HG2); 16 mL CH_2Cl_2 ; 308 K. BQ: benzoquinone = 0.1 eq. and phenol= 1 eq. (both to -[C_4H_6]- units 1,4-PB).

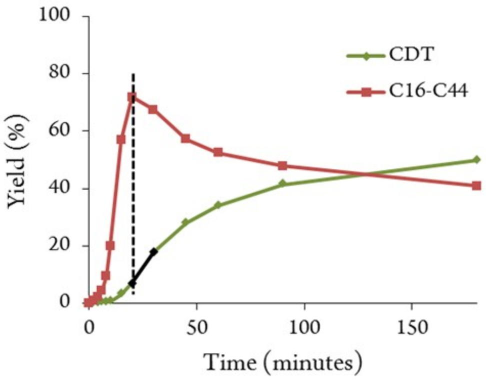

Figure S7. Kinetic analysis of the formation of CDT in time. The maximum formation rate of CDT (small black line in the green curve) is attained at the maximum yield of C16-C44 macrocycles (dashed black line). Reaction conditions: 0.17 M -[C_4H_6]- (PB-250 000); 0.5 mol% Ru (HG2); 16 mL CH_2Cl_2 ; 308 K.

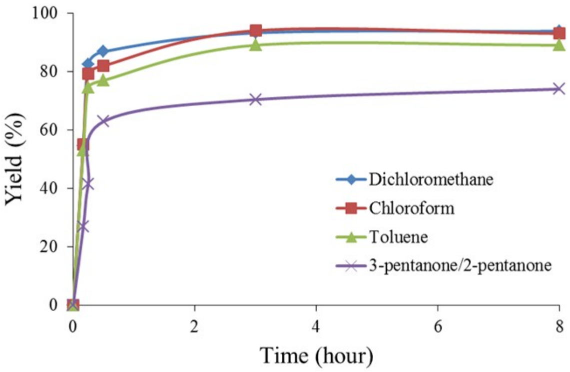

Figure S8. Yield of C12-C44 macrocycles in time from depolymerization of PB-250 000 with HG2 in different solvents. Reaction conditions: 0.17 M -[C_4H_6]- (PB-250 000) ; 0.5 mol% Ru (HG2) ; 16 mL solvent ; 308 K.

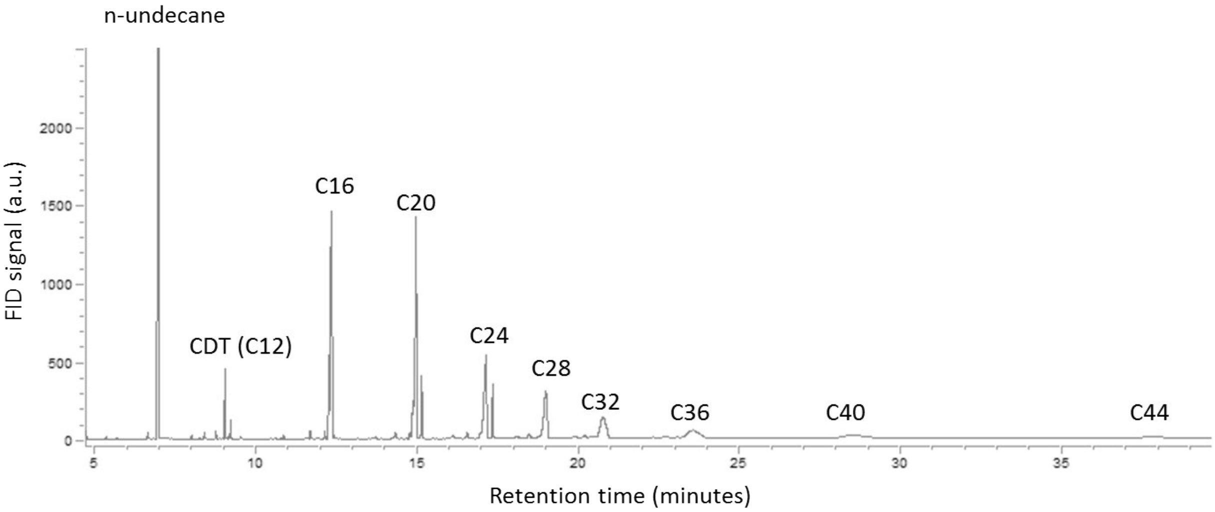

Figure S9. GC chromatogram after depolymerization of PB-250 000 with complex **9** after 8h of reaction. Reaction conditions: 0.17 M -[C_4H_6]- (PB-250 000); 0.5 mol% Ru (complex **9**) ; 16 mL CH_2Cl_2 ; 308 K.

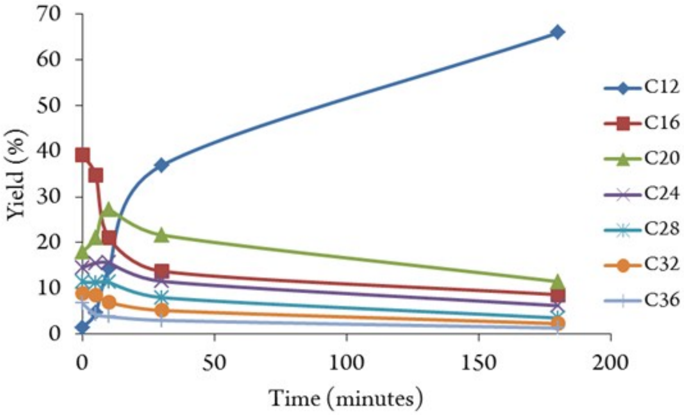

Figure S10. Conversion of C16-C44 cyclic oligomers in presence of a second-generation Ru metathesis catalyst to CDT (C12). Reaction conditions: 0.17 M (C16-C44) macrocycles; 0.5 mol% Ru (HG2); 16 mL CH_2Cl_2 ; 308 K.

Table S1. Distribution of C16-C32 cyclic oligomers after ROMP of *cis*-cyclooctene.

	Conversion (%)	C16 (%)	C24 (%)	C32 (%)
Hoveyda-Grubbs II (ref 40)	> 98	26	31	20
Grubbs I (ref 20)	> 98	27	30	19

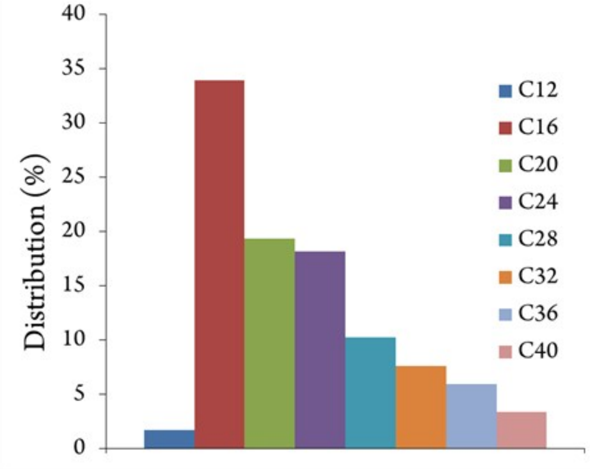

Figure S11. Distribution of C12-C44 cyclic oligomers after depolymerization of PB-250 000 with complex **9** at 333K. Reaction conditions: 0.17 M -[C_4H_6]- (PB-250 000); 0.5 mol% Ru (complex **9**); 16 mL CH_2Cl_2 ; 333 K.