

Effective Regulation of Polycaprolactone Molecular Weight and Oligomers Content Using Tetraphenyltin Catalyst

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Submitted date: 16/08/2020 • Posted date: 17/08/2020

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Citation information: Gong, Caihong; Li, Jinxia; Yi, Chunwang; Qu, Shuanglin (2020): Effective Regulation of Polycaprolactone Molecular Weight and Oligomers Content Using Tetraphenyltin Catalyst. ChemRxiv.

Preprint. <https://doi.org/10.26434/chemrxiv.12813773.v1>

There is a lack of effective approaches that produce polycaprolactone materials (PCL) with a high molecular weight, narrow polymer dispersity index (PDI), and fewer formation of oligomers. The immigration of the remained oligomers predominantly causes poor PCL quality and induces odor release. This limits the extensive application of PCL materials. This study investigates the effects of different catalysts and loadings on the PCL performance along with the formation of oligomers in detail. The oligomers were successfully separated using gel permeation chromatography (GPC). This was followed by a quantitative and qualitative identification using high-resolution mass spectrometry (HRMS) and low field nuclear magnetic (L-field NMR) analysis. The results show that tetraphenyltin is an effective catalyst to promote the reaction and produce high-performance PCL that possesses the highest Mn (65000), narrowest PDI (1.37), and the lowest content of oligomers (7.466 wt.%). Density functional theory (DFT) studies that were combined with characterizing key intermediates verified that an anhydride bond was formed close to the end hydroxyl group in the PCL chain because of the special catalytic mechanism. This unusual chemical structure successfully inhibited the chain from being broken by the “back-biting” behavior, which is helpful for lowering the content of oligomers. This study can provide a scalable synthetic approach to creating high-performance polymers.

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Supporting Information for

Effective Regulation of Polycaprolactone Molecular Weight and Oligomers Content Using Tetraphenyltin Catalyst

Caihong Gong, Jinxia Li, Chunwang Yi*, Shuanglin Qu*

Table of contents:

Supplementary Information for Experimental Studies	Pages S2-S6
Supplementary Information for DFT Calculations	Pages S7-S53

Supplementary Information for Experimental Studies

Materials

Tetraphenyl tin, triphenyltin chloride, dimethyldiphenyltin, tetramethyltin and ϵ -caprolactone used in this experiment were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. And the chloroform (chromatographic pure) was provided by Sinopharm Chemical Reagent Co., Ltd. Commercial PCL was from the solvay brand of dongguan zhanpeng polymer material co., LTD.

Instruments and characterizations

The functional groups and types of bonding in the samples were determined by Thermo Fisher Nicolet NEXUS series infrared spectrum equipped with attenuated total reflectance (ATR), the infrared spectra of the samples were recorded in the range of frequency of 600 - 4000 cm^{-1} .

3-5 mg Polymer samples were dissolved in deuterated-chloroform and ^1H NMR spectra were recorded with a BRUKER AVANCE-500 series ^1H NMR spectrometer.

The relative molecular weight (M_n and M_w) and polydispersity index (PDI) of PCL was measured by GPC (ALLTECH Gel Permeation) equipped with a RI2000 refractive index detector and Shodex DVB column (1000Å, 300 mm 3×5mm), a PLgel 5 μm MIXED-C 300 mm × 7.5 mm column. Chloroform was used as the eluent at a flow rate of 0.6 mL min^{-1} . During testing, the column temperature was maintained at 35°C. The calibration curve was fitted with standards (polystyrene). All acquired products were numbered as A~R in alphabetical order.

Low field NMR technique was performed to test the T2 relaxation time of the polymer sample by CPMG sequence. After the inversion of multi-component, the "long-chain segment" and "small molecule" in the polymer were calculated according to the proportion of different peak areas. The content of all samples were measured on a VTMR20-010V-I spectrometer (Suzhou Niuman Analytical Instruments Co., Ltd.) with a 10-mm hydrogen test probe under conditions of primary frequency of 21 MHz, magnet strength of 0.5 T and magnet temperature of 35 $\pm$ 0.01 °C.

HRMS test: 20mg of samples was dissolved in dichloromethane and tested by brook solanX 70 ft-ms model. The tested ion source was ESI and positive ionization mode scan spectra were taken.

The computerized polarized light microscope and N-type thermal table prepared by Shanghai changfang optical instrument co., LTD are used to observe the crystallization and melting temperature of samples.

Mechanical tests were carried out by universal tensile testing machine (WDW3020) using ASTM D638-2006 method at room temperature with a crosshead speed of 200 mm/min and 20kN. The modulus of each sample was determined by linearly fitting the elastic portion of the stress-strain curve. Each test was in five repeats and the results were averaged.

Table S1. Process parameters for PCL preparation

Sample	ϵ -caprolactone (g)	catalyst type	catalyst (g)	time (h)	temperature (°C)
1	50	tetramethyltin	0.5	10	200
2	50	dimethyldiphenyltin	0.5	10	200
3	50	triphenyltin chloride	0.5	10	200
4	50	tetraphenyl tin	0.5	10	200
5	50	tetraphenyl tin	0.05	10	200
6	50	tetraphenyl tin	0.25	10	200
7	50	tetraphenyl tin	2.5	10	200
8	50	tetraphenyl tin	5	10	200
9	50	tetraphenyl tin	0.5	2	200
10	50	tetraphenyl tin	0.5	4	200
11	50	tetraphenyl tin	0.5	6	200
12	50	tetraphenyl tin	0.5	8	200
13	50	tetraphenyl tin	0.5	12	200
14	50	tetraphenyl tin	0.5	14	200
15	50	tetraphenyl tin	0.5	10	120
16	50	tetraphenyl tin	0.5	10	140
17	50	tetraphenyl tin	0.5	10	160
18	50	tetraphenyl tin	0.5	10	180
19	50	tetraphenyl tin	0.5	10	220
20	50	tetraphenyl tin	0.5	10	240

Table S2. GPC (gel chromatography) test data

Sample	M _w	M _n	PDI
S	86000	60000	1.43
1	68000	25900	2.63
2	69000	29700	2.32
3	81800	38500	2.12
4	89700	65400	1.37
5	13000	4800	2.70
6	25400	9600	2.65
7	30100	15300	1.97
8	51500	26000	1.98
9	-	-	-
10	-	-	-
11	5400	2100	2.57
12	9600	4100	2.34
13	63600	30400	2.09
14	16000	6600	2.42
15	-	-	-
16	-	-	-
17	-	-	-
18	76500	31000	2.47
19	73700	30600	2.41
20	45600	15300	2.98

S: Commercial PCL; The GPC tests of the liquid samples 9 and 10 , and the wax-alike

samples 15, 16 and 17, were not conducted because they do not have good mechanical properties.

Table S3. Low field ¹H-NMR test data

Sample	Polymer content A(%)	oligomerB(%)	oligomerC(%)	All oligomers(%)
S	91.706	7.651	0.643	7.466
1	87.48	11.56	0.974	12.22
2	89.702	9.482	0.817	10.298
3	89.728	9.411	0.861	10.272
4	92.534	6.825	0.641	7.466
5	80.32	19.11	0.57	19.68
6	81.48	18.052	0.468	18.52
7	82.357	17.134	0.509	17.643
8	84.364	14.982	0.654	15.636
9	-	-	-	-
10	-	-	-	-
11	79.658	19.653	0.689	20.342
12	87.986	10.698	1.316	12.014
13	88.393	10.962	0.645	11.607
14	80.657	18.954	0.389	19.343
15	-	-	-	-
16	-	-	-	-
17	-	-	-	-
18	89.865	9.067	1.068	10.135
19	88.951	10.004	1.045	11.049
20	80.368	18.369	1.263	19.632

S: Commercial PCL; The tests of the liquid samples 9 and 10 , and the wax-alike samples 15, 16 and 17, were not conducted because they do not have good mechanical properties.

Figure S1. Back-bite mechanism in open-loop polymerization. ^[ref. 23]

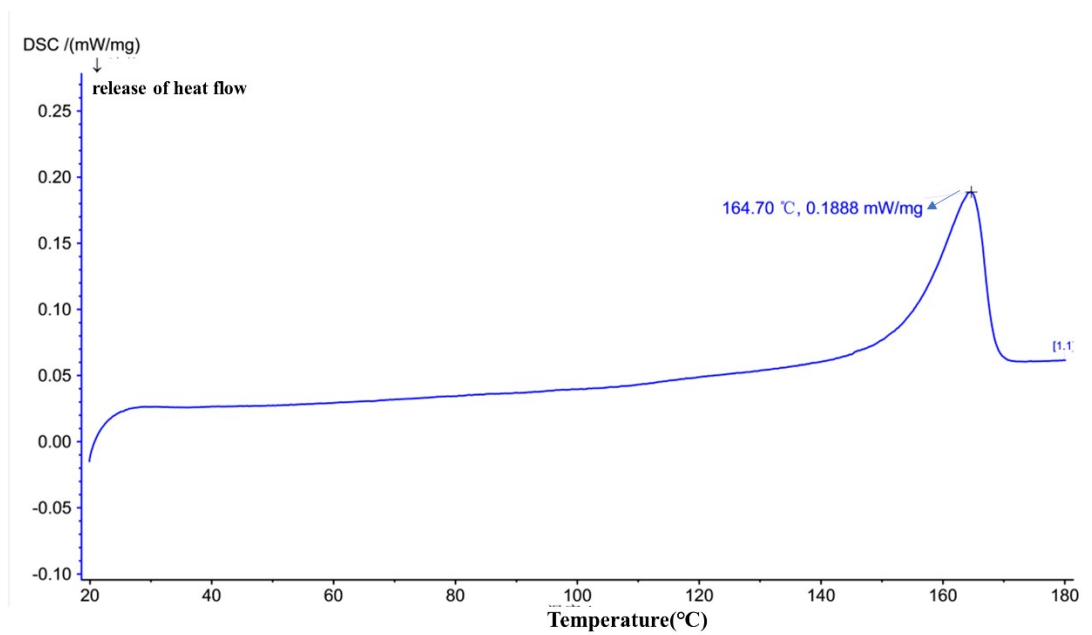


Figure S2. DSC curve of intermediate

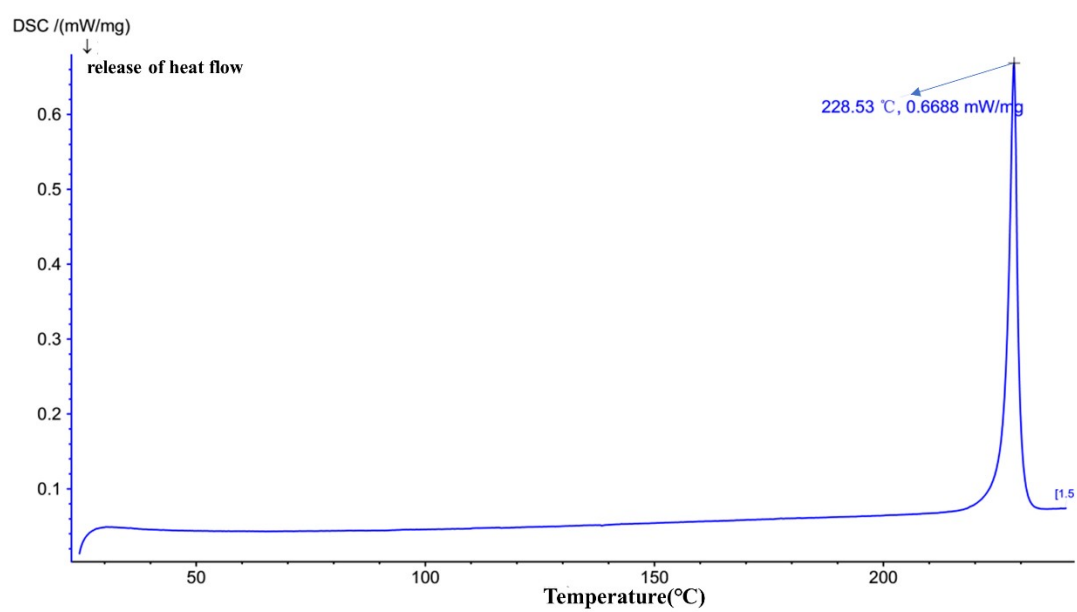


Figure S3. DSC curve of tetraphenyltin

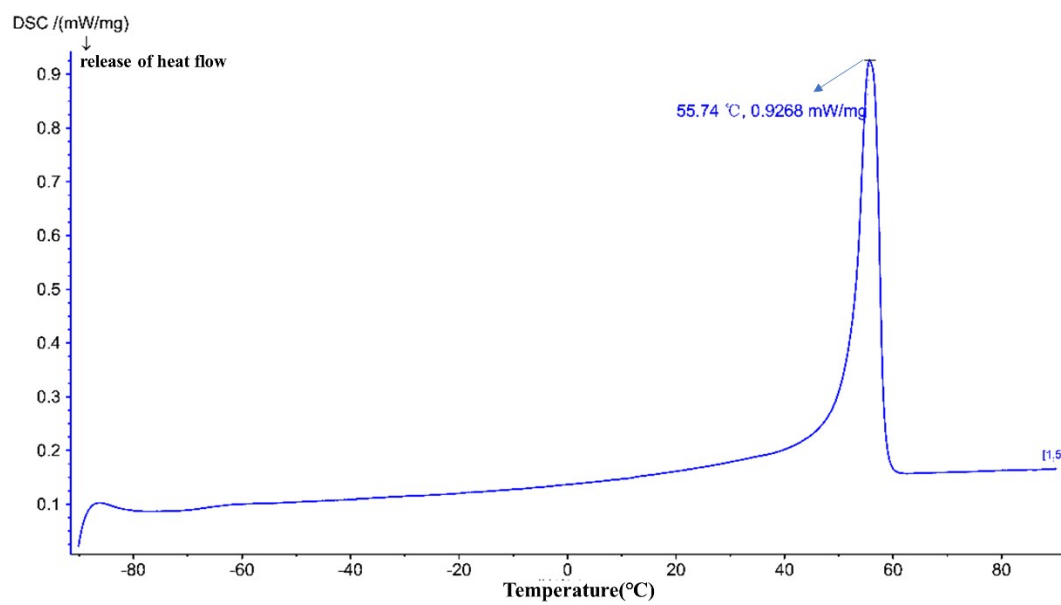


Figure S4. DSC curve of PCL

Supplementary Information for DFT Calculations

1. Computational Methods

All the structures were optimized at gas phase under B3LPY¹-D3BJ²/BSI level using GAUSSIAN 09 program,³ where BSI represents a basis set combination of SDD⁴ for Sn and 6-31G(d)⁵ for main group atoms. Analytic harmonic vibrational frequencies were computed to verify the nature of all optimized stationary points as either minima or transition-state (TS) structures, having zero and one imaginary frequencies, respectively, and to compute thermal contributions to 298.15 K, 1 atm free energies. Improved energies were computed at M06/BSII-SMD(cyclohexanone) single-point calculations. Basis set BSII is a combination of SDD for Sn and 6-311++G(d,p)⁶ for all other atoms. In the present study, we correct all solute free energies for the change in standard state concentration from 1 atm to 1 M (equal to $RT \ln(24.5)$, or 1.9 kcal/mol).

References

1. (a) Lee, C. T.; Yang, W. T.; Parr, R. G., DEVELOPMENT OF THE COLLE-SALVETTI CORRELATION-ENERGY FORMULA INTO A FUNCTIONAL OF THE ELECTRON-DENSITY. *Phys. Rev. B* **1988**, 37, 785-789; (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H., RESULTS OBTAINED WITH THE CORRELATION-ENERGY DENSITY FUNCTIONALS OF BECKE AND LEE, YANG AND PARR. *Chem. Phys. Lett.* **1989**, 157, 200-206; (c) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J., AB-INITIO CALCULATION OF VIBRATIONAL ABSORPTION AND CIRCULAR-DICHROISM SPECTRA USING DENSITY-FUNCTIONAL FORCE-FIELDS. *J. Phys. Chem.* **1994**, 98, 11623-11627.
2. Grimme, S.; Ehrlich, S.; Goerigk, L., Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011**, 32, 1456-1465.
3. Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., *Gaussian 09*, Revision A.01; Gaussian, Inc., Wallingford CT, 2009.
4. (a) Roy, L. E.; Hay, P. J.; Martin, R. L., Revised basis sets for the LANL effective core potentials. *J. Chem. Theory Comput.* **2008**, 4, 1029-1031; (b) Andrae, D.; Haussermann, U.; Dolg, M.; Stoll, H.; Preuss, H., ENERGY-ADJUSTED ABINITIO PSEUDOPOTENTIALS FOR THE 2ND AND 3RD ROW TRANSITION-ELEMENTS. *Theor. Chem. Acc.* **1990**, 77, 123-141.
5. (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A., Self-Consistent Molecular Orbital Methods. XII.

Further Extensions of Gaussian---Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *J. Chem. Phys.* **1972**, 56, 2257-2261; (b) Francel, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A., Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements. *J. Chem. Phys.* **1982**, 77, 3654-3665.

6. (a) Wachters, A. J. H., Gaussian Basis Set for Molecular Wavefunctions Containing Third-Row Atoms. *J. Chem. Phys.* **1970**, 52, 1033-1036; (b) Francel, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A., Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements. *J. Chem. Phys.* **1982**, 77, 3654-3665.

2. Additional computational results mentioned in the main text.

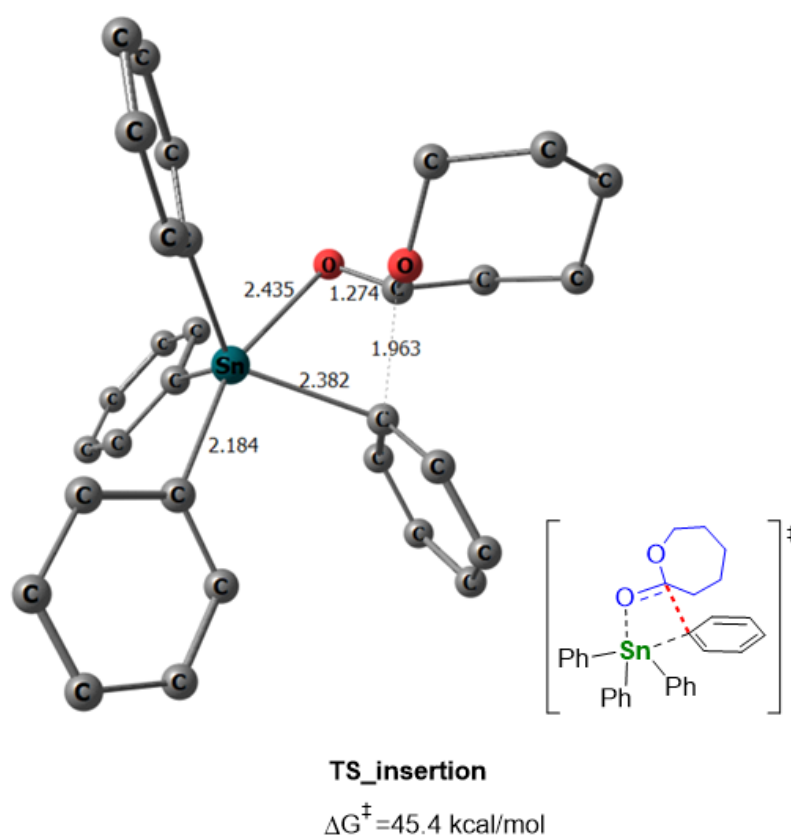


Figure S5. Transition state for the insertion of phenyl group to the coordinated ester. Hydrogen atoms were hidden for clarity.

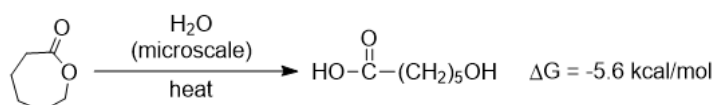


Figure S6. Thermodynamics of the hydrolysis of caprolactone.

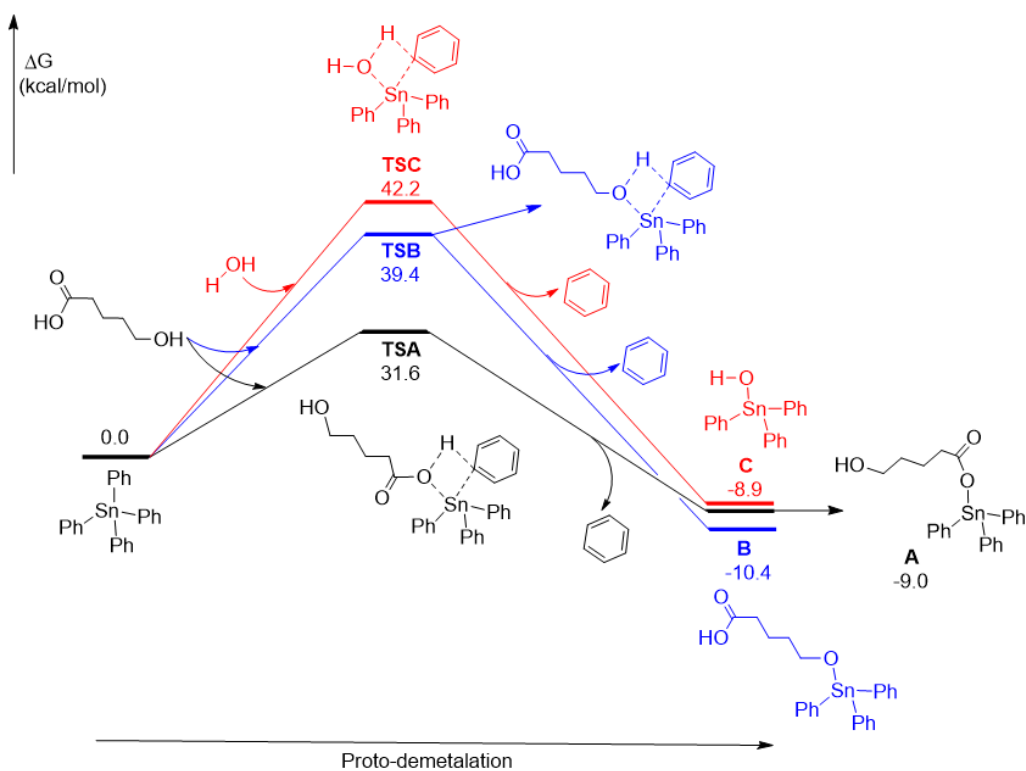


Figure S7. Free energy profiles for proto-demetalation step (release of benzene ring).

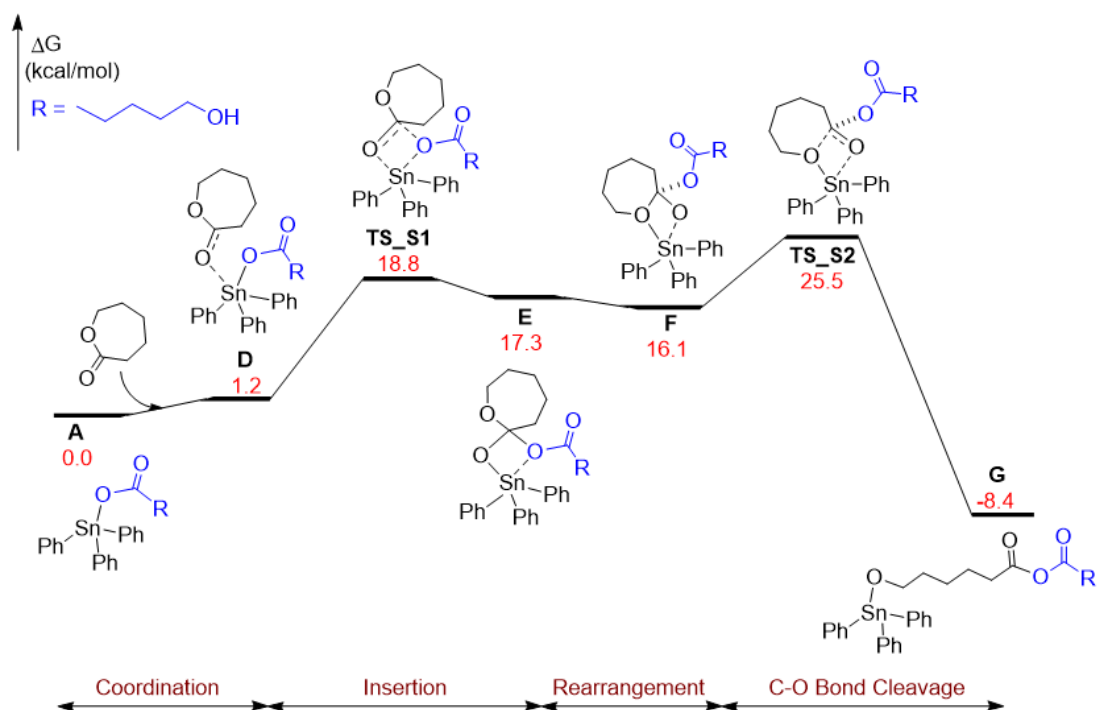


Figure S8. Free energy profile of the formation of Tin-alkoxide complex.

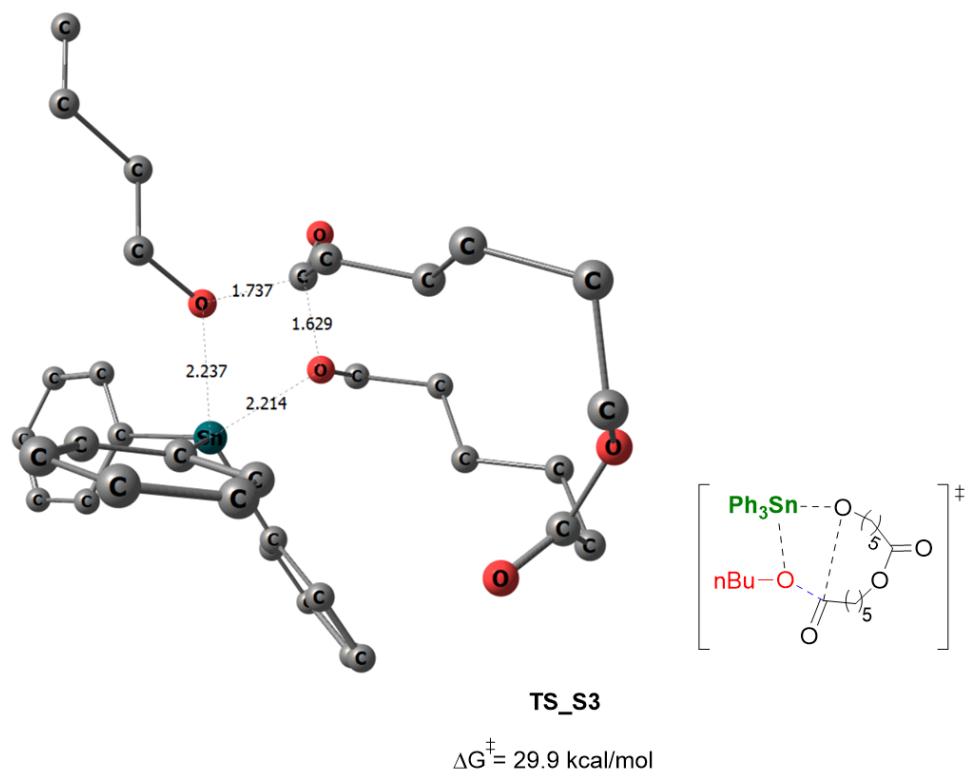


Figure S9. Transition state for the “back-biting” of the internal ester bond at the Sn-O bond. The polymer chain is simplified by the -O-*n*Bu group. Hydrogen atoms were hidden for clarity.

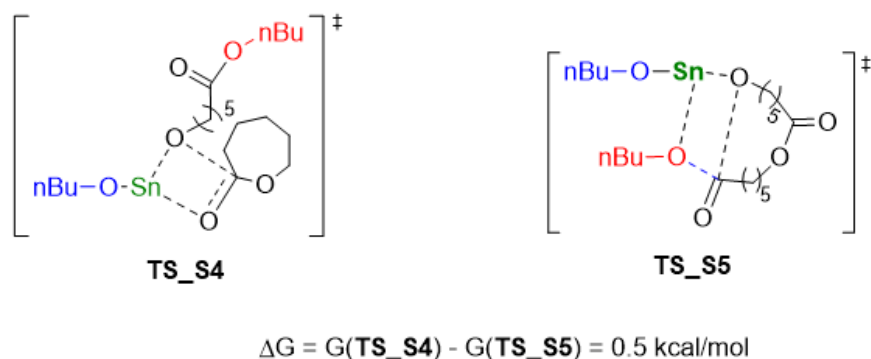


Figure S10. Relative free energies for the transition states of insertion and back-biting of a previous Sn(II) catalytic system. The polymer chain is simplified by the -O-*n*Bu group.

3. Energies and Cartesian coordinates

The followings are SCF energies (in au), free energies (in au) and Cartesian coordinates for all optimized structures.

ε-caprolactone

SCF energy: -385.128303

Free energy: -384.847150

C	1.58173300	0.73691000	-0.09127100
C	0.41100000	1.70254600	0.19978600
C	-0.96414200	1.32488800	-0.41518400
C	1.45717200	-0.65394300	0.57433800
C	-1.21110700	-0.12063800	-0.07101900
C	0.58040800	-1.63604200	-0.21914700
H	1.71226200	0.62179200	-1.17484800
H	0.28869200	1.78163200	1.28778300
H	-0.92912700	1.43937900	-1.50297700
H	1.04791900	-0.52839400	1.58473300
H	0.15100900	-2.40883100	0.42700300
H	2.49387300	1.21556800	0.28438300
H	0.67722100	2.70289300	-0.16083600
H	-1.75120900	1.96125500	-0.00286800
H	2.45082300	-1.10165300	0.69605500
H	1.14649300	-2.11573100	-1.02097800
O	-0.46394000	-0.91913800	-0.90441300
O	-1.83835400	-0.54214100	0.86910400

Tetraphenyltin

SCF energy: -930.050660

Free energy: -929.153225

Sn	-0.00004000	0.00027900	0.00021600
C	1.26420400	-1.24563700	-1.20829500
C	0.88679100	-1.60125800	-2.51246000
C	2.47917500	-1.73707300	-0.70474600
C	1.69608800	-2.43168800	-3.29017000
H	-0.04329000	-1.22242200	-2.93104600
C	3.29102200	-2.56858000	-1.47975000
H	2.80541000	-1.46217400	0.29614000
C	2.89855400	-2.91775100	-2.77303000
H	1.39116300	-2.69718200	-4.29911000
H	4.22928100	-2.94071900	-1.07641000
H	3.52964600	-3.56358100	-3.37765500
C	1.26968800	1.24207500	1.20721200
C	0.89471600	1.59944200	2.51160300
C	2.48593200	1.72903400	0.70240400
C	1.70765400	2.42723300	3.28832600
H	-0.03631000	1.22402400	2.93117100
C	3.30142300	2.55789100	1.47642400
H	2.81029900	1.45266300	-0.29867700
C	2.91136900	2.90886500	2.76994300
H	1.40458700	2.69411800	4.29745800

H	4.24063100	2.92657100	1.07211700
H	3.54529000	3.55264900	3.37378900
C	-1.26811500	-1.20579600	1.24458200
C	-0.89454000	-2.51144700	1.59877700
C	-2.48176200	-0.69931000	1.73625600
C	-1.70630300	-3.28779400	2.42808000
H	0.03443700	-2.93225200	1.21968200
C	-3.29606500	-1.47294900	2.56663000
H	-2.80506100	0.30282100	1.46242000
C	-2.90741200	-2.76775700	2.91441200
H	-1.40435200	-4.29791100	2.69249200
H	-4.23327100	-1.06734700	2.93896500
H	-3.54041100	-3.37131400	3.55937200
C	-1.26585100	1.20983200	-1.24311400
C	-0.88718600	2.51292100	-1.60132300
C	-2.48315100	0.70786800	-1.73036700
C	-1.69754600	3.29111600	-2.43026000
H	0.04472500	2.93032800	-1.22569500
C	-3.29607300	1.48336700	-2.56036400
H	-2.81034000	-0.29211400	-1.45333000
C	-2.90234900	2.77554200	-2.91219400
H	-1.39161400	4.29920600	-2.69781500
H	-4.23614800	1.08126500	-2.92924900
H	-3.53425700	3.38054100	-3.55687300

Water

SCF energy: -76.407598

Free energy: -76.422204

O	0.00000000	0.00000000	0.11942600
H	0.00000000	0.76260200	-0.47770600
H	0.00000000	-0.76260200	-0.47770600

6-hydroxyhexanoic acid

SCF energy: -461.559977

Free energy: -461.275286

C	2.91012200	0.13767300	-0.00000400
C	1.61567100	-0.64297800	-0.00005900
H	1.62537100	-1.30847300	-0.87370600
H	1.62538400	-1.30864000	0.87345900
C	0.37893700	0.25356200	0.00002700
H	0.41191700	0.91380000	-0.87483700
H	0.41195400	0.91362500	0.87502800

C	-0.92477200	-0.54930300	-0.00003000
H	-0.94666900	-1.21051700	0.87887300
H	-0.94672300	-1.21033000	-0.87907100
C	-2.16828700	0.34378100	0.00009500
H	-2.16185900	0.99970000	-0.87984100
H	-2.16183300	0.99953000	0.88015200
C	-3.46522500	-0.45225600	0.00001000
H	-3.49917500	-1.10632400	0.88784200
H	-3.49891000	-1.10653200	-0.88769600
O	3.01675100	1.34406500	0.00002500
O	3.98845700	-0.68745900	0.00002000
H	4.77078200	-0.10407900	-0.00003400
O	-4.54718200	0.47097300	-0.00029100
H	-5.37312000	-0.03526900	0.00156500

Benzene

SCF energy: -232.262723

Free energy: -232.0466010

C	-1.33846600	-0.39754200	0.00000400
C	-0.32483700	-1.35790600	0.00006600
C	1.01349800	-0.96036500	-0.00005400
C	1.33843100	0.39765300	0.00000700
C	0.32495000	1.35787600	0.00006000
C	-1.01357700	0.96028600	-0.00005600
H	-2.37973500	-0.70694700	-0.00006500
H	-0.57774600	-2.41433100	0.00008000
H	1.80212100	-1.70738400	-0.00015000
H	2.37977200	0.70679300	0.00000900
H	0.57761100	2.41435300	0.00001600
H	-1.80202000	1.70750500	-0.00006000

Tin-alkoxide (Active catalyst)

SCF energy: -1544.504292

Free energy: -1543.222839

Sn	-2.82982000	0.20331500	0.07731500
C	-4.03016900	1.17282300	-1.40332100
C	-3.67783600	2.42722200	-1.92352200
C	-5.17575400	0.52989900	-1.89632300
C	-4.46152900	3.03413600	-2.90704700
H	-2.78207700	2.93549000	-1.57192200
C	-5.95989600	1.13595400	-2.87966000
H	-5.44436400	-0.45330500	-1.51835300

C	-5.60459300	2.38904300	-3.38309000
H	-4.17975100	4.00605600	-3.30348300
H	-6.84517100	0.63010500	-3.25594900
H	-6.21491800	2.86037700	-4.14871800
C	-3.14333100	0.61108800	2.14835100
C	-2.75774300	1.82581300	2.73488800
C	-3.71155800	-0.38561900	2.95659900
C	-2.94326900	2.04459900	4.10125300
H	-2.30471200	2.61027800	2.13180000
C	-3.89926200	-0.16569400	4.32251400
H	-3.99762200	-1.33599500	2.51363200
C	-3.51630100	1.04887900	4.89471700
H	-2.64008200	2.98855100	4.54623700
H	-4.34030000	-0.94285000	4.94105900
H	-3.66063600	1.21853500	5.95826000
C	-0.76041400	0.43550100	-0.44459500
C	0.23418300	0.43328700	0.54610900
C	-0.37037200	0.46127000	-1.79230100
C	1.58760800	0.44132700	0.20196100
H	-0.04615300	0.40973300	1.59696900
C	0.98194800	0.47072000	-2.14180200
H	-1.12331400	0.47540200	-2.57739500
C	1.95898500	0.45526400	-1.14486200
H	2.34728800	0.41269400	0.97705200
H	1.27289300	0.48692300	-3.18886100
H	3.00943300	0.45966100	-1.41973500
C	2.34605700	-4.14735600	-0.95224700
C	1.20019900	-3.52685400	-0.12251500
C	-0.15122300	-3.58893300	-0.83926800
C	3.65429000	-3.81426200	-0.29368600
C	-1.26888600	-2.97562900	0.01227100
C	-2.51897100	-2.59639100	-0.78979200
H	2.24046800	-5.23472900	-1.00120000
H	1.14796600	-4.03893500	0.84585900
H	-0.39274200	-4.62522900	-1.11344200
H	-1.54605800	-3.64299100	0.83763900
H	2.33268900	-3.73663300	-1.96690300
H	1.43571900	-2.47743600	0.08950100
H	-0.06808000	-3.02674100	-1.78033000
H	-0.87740000	-2.06295200	0.47410100
H	-2.20119500	-2.15042700	-1.74894500
H	-3.09760600	-3.49571500	-1.04280200
O	4.24339000	-4.45224400	0.53110000
O	-3.37828200	-1.72483900	-0.07325300

O	4.15003100	-2.58162600	-0.76649200
C	4.55437500	-1.62067800	0.13559300
O	4.14499400	-1.56767200	1.26681000
C	5.51810400	-0.65640800	-0.51366200
H	6.49165400	-1.16632700	-0.55884500
H	5.21617700	-0.50706400	-1.55690500
C	5.63751400	0.66756800	0.24073200
H	4.65778900	1.16183600	0.26567100
H	5.89937800	0.46206900	1.28451700
C	6.66806500	1.60881600	-0.38814700
H	6.40305600	1.79118100	-1.44010200
H	7.65098100	1.11556100	-0.40184500
C	6.77294400	2.94469800	0.35209700
H	5.79880300	3.45044800	0.35696600
H	7.04349500	2.77414700	1.40187900
C	7.80004500	3.88207400	-0.26623600
H	7.53872200	4.07534300	-1.32061000
H	8.79272700	3.40092600	-0.25971700
O	7.80606400	5.08547200	0.49123000
H	8.46509200	5.68059500	0.10396600

Int_1

SCF energy: -1929.66859

Free energy: -1928.066578

C	4.92983500	1.19272000	1.84223000
C	3.95808100	2.37057200	1.62376900
C	4.57746300	3.56853300	0.90015900
C	5.17225200	0.35565600	0.60043500
C	5.16545900	3.23510100	-0.47593100
C	6.32013200	2.23596600	-0.43594500
H	5.88971600	1.56519200	2.22653000
H	3.09828100	2.00391500	1.05887600
H	5.37083200	4.00424900	1.52609700
H	4.39292800	2.82558200	-1.13626000
H	4.51622800	0.50677400	2.58267000
H	3.59517000	2.68879800	2.60762900
H	3.81394500	4.34812900	0.78395800
H	5.53839200	4.15736600	-0.93994700
H	6.91304100	2.29677000	-1.35074000
H	6.98942400	2.42982400	0.41267200
O	4.76182600	-0.78576400	0.49056000
O	5.89118800	0.86181900	-0.41716000
Sn	1.84798000	-0.96923700	-0.16305300

C	2.57682800	-2.65064600	-1.26972400
C	1.63108500	-3.60687000	-1.67645000
C	3.92042300	-2.82626900	-1.63575700
C	2.01864600	-4.71971100	-2.42580700
H	0.58234100	-3.48485400	-1.41630100
C	4.30367100	-3.93683200	-2.39021600
H	4.66149600	-2.10257300	-1.31639200
C	3.35685600	-4.88421900	-2.78485900
H	1.27688100	-5.45359100	-2.73022900
H	5.34652900	-4.06306200	-2.66974200
H	3.66103900	-5.74778400	-3.37065400
C	2.03825800	-0.88284700	1.96646200
C	2.76737000	-1.84768400	2.67608500
C	1.46258100	0.18133900	2.67633700
C	2.91960200	-1.74991600	4.05990900
H	3.24574300	-2.66504300	2.14412600
C	1.61762100	0.28606000	4.06108200
H	0.90263400	0.95194100	2.15158200
C	2.34809300	-0.68025500	4.75391300
H	3.49119300	-2.50250100	4.59662700
H	1.17148900	1.12072700	4.59537700
H	2.47167500	-0.60139600	5.83064300
C	-0.26766900	-0.86221800	-0.61548500
C	-1.21180600	-0.61678200	0.39429800
C	-0.72192900	-0.92403200	-1.94343200
C	-2.56002300	-0.41097900	0.09086100
H	-0.89493300	-0.57174900	1.43319600
C	-2.06852000	-0.72226100	-2.25530100
H	-0.02149400	-1.13604500	-2.74849900
C	-2.98713700	-0.45695300	-1.23792200
H	-3.26824600	-0.19405000	0.88478200
H	-2.40017400	-0.77040900	-3.28941100
H	-4.03233500	-0.29311200	-1.48287700
C	-2.78465100	3.89545700	-1.83000400
C	-1.65603500	3.29121600	-0.96518200
C	-0.40081600	2.96567000	-1.77831800
C	-4.04945800	3.92576000	-1.02018800
C	0.70336200	2.36554600	-0.90006200
C	1.76164300	1.58969100	-1.69216500
H	-2.53214100	4.91534900	-2.13370800
H	-1.42224100	3.98880200	-0.15167700
H	-0.03942900	3.86146500	-2.30236500
H	1.18770400	3.14256300	-0.29394200
H	-2.93647700	3.27927400	-2.72174700

H	-2.01586000	2.36859200	-0.49584800
H	-0.67465300	2.23631100	-2.55292600
H	0.23561400	1.66872100	-0.19687400
H	1.25451000	0.99110100	-2.46542600
H	2.41843000	2.29069000	-2.22844000
O	-4.43917900	4.80280600	-0.30353300
O	2.58431400	0.78611300	-0.86666300
O	-4.77762300	2.73054900	-1.18848000
C	-5.21116400	2.03524000	-0.07931300
O	-4.69417800	2.13694500	1.00334700
C	-6.36355300	1.12827400	-0.44016200
H	-7.26484400	1.75891600	-0.45698300
H	-6.22917800	0.77729600	-1.46959300
C	-6.53910000	-0.03261800	0.53905800
H	-5.63976700	-0.66159700	0.52081500
H	-6.61154800	0.36636500	1.55680600
C	-7.76678200	-0.88851800	0.21729900
H	-7.68825300	-1.26860600	-0.81192100
H	-8.66699600	-0.25705000	0.24219200
C	-7.93532000	-2.06252900	1.18526400
H	-7.04616300	-2.70535700	1.15701600
H	-8.02311800	-1.69282400	2.21482000
C	-9.15689000	-2.91401400	0.87120000
H	-9.07987900	-3.30850700	-0.15627100
H	-10.06525400	-2.28931300	0.91295400
O	-9.21270600	-3.96787200	1.82422900
H	-9.99082100	-4.51010900	1.62683700

TS1

SCF energy: -1929.644335

Free energy: -1928.038933

C	4.64333900	1.25557300	1.27241900
C	4.27375700	2.67924100	1.70161200
C	5.14194000	3.78348800	1.09412900
C	4.23152400	0.78612100	-0.11664200
C	5.09076300	3.85285500	-0.43392300
C	5.55415100	2.57830800	-1.13592000
H	5.73023200	1.10053200	1.34722900
H	3.21835800	2.85024400	1.46628000
H	6.18632700	3.62885800	1.40330800
H	4.07850800	4.09947500	-0.77782800
H	4.18782600	0.53717600	1.95659400
H	4.36075800	2.73056500	2.79387600

H	4.83873100	4.75293300	1.50893700
H	5.74282000	4.66682600	-0.77852800
H	5.76760900	2.78686000	-2.18687500
H	6.47804500	2.20080400	-0.67794400
O	4.16906500	-0.48160600	-0.31147700
O	4.59125500	1.51407900	-1.21008300
Sn	2.02921800	-1.09363600	-0.08048800
C	2.50271600	-2.76477400	-1.35200000
C	1.45384600	-3.60443400	-1.75971800
C	3.81207900	-3.08026200	-1.74378900
C	1.70672300	-4.73887000	-2.53451600
H	0.42872000	-3.37064900	-1.48167500
C	4.06501300	-4.21241400	-2.52091200
H	4.62695200	-2.42929900	-1.44638400
C	3.01419700	-5.04326800	-2.91584300
H	0.88508900	-5.38066600	-2.84225800
H	5.08332800	-4.44559900	-2.82189000
H	3.21372900	-5.92381100	-3.52106500
C	2.02335800	-1.45067300	2.02821100
C	2.26126300	-2.73030700	2.55037200
C	1.75254400	-0.39900500	2.91883800
C	2.22915600	-2.95579900	3.92846700
H	2.47632300	-3.56020700	1.88066700
C	1.71994900	-0.62195500	4.29711900
H	1.57602300	0.60223100	2.53334900
C	1.95815100	-1.90161400	4.80258300
H	2.41661200	-3.95224400	4.31993900
H	1.50887000	0.20063300	4.97562900
H	1.93223600	-2.07672000	5.87476200
C	-0.03006700	-0.68098000	-0.66935200
C	-1.00143900	-0.40531400	0.30543100
C	-0.41090300	-0.60944300	-2.01847500
C	-2.30306500	-0.04104600	-0.04959700
H	-0.74128600	-0.46065300	1.36044500
C	-1.70904600	-0.24228900	-2.38400200
H	0.31114100	-0.84431500	-2.79819400
C	-2.65395800	0.05194800	-1.39861400
H	-3.03166400	0.19064800	0.72166800
H	-1.98196600	-0.18304700	-3.43474300
H	-3.65783600	0.35272700	-1.68425800
C	-2.78087400	4.26513700	-1.29257900
C	-1.72850200	3.66340500	-0.33187400
C	-0.41637600	3.33132200	-1.04511700
C	-4.12781200	4.21387700	-0.63065200

C	0.60672000	2.68755700	-0.10213400
C	1.74323400	1.99693300	-0.85595900
H	-2.53670600	5.30490500	-1.52811000
H	-1.56236200	4.36355400	0.49549900
H	0.00140900	4.23161300	-1.51803600
H	1.01055400	3.42698500	0.60234000
H	-2.81025900	3.68218400	-2.21814400
H	-2.12588600	2.74389700	0.11041500
H	-0.63943400	2.62351400	-1.85454900
H	0.09753300	1.92637000	0.49542600
H	1.33462800	1.48838300	-1.73786000
H	2.48543700	2.71465800	-1.22269200
O	-4.62506300	5.03084800	0.08865100
O	2.41621300	1.06180000	-0.02320700
O	-4.80536100	3.01336500	-0.95342500
C	-5.18492800	2.16496400	0.06001600
O	-4.70066700	2.20268400	1.16367900
C	-6.23150100	1.18872600	-0.42322100
H	-7.20019400	1.70449700	-0.34656900
H	-6.07737600	1.00063200	-1.49146200
C	-6.25070700	-0.10944800	0.38538500
H	-5.28491800	-0.61856200	0.27441000
H	-6.34873500	0.13413200	1.44900600
C	-7.37677700	-1.05135900	-0.04805100
H	-7.27522500	-1.27367600	-1.12049200
H	-8.34398300	-0.54065800	0.06842700
C	-7.38685600	-2.35953800	0.74714000
H	-6.42883100	-2.88129100	0.62682100
H	-7.49747300	-2.14875400	1.81845700
C	-8.50562500	-3.29895100	0.32085900
H	-8.40181500	-3.53685600	-0.75146100
H	-9.48017000	-2.79831100	0.45050400
O	-8.42002100	-4.47282400	1.11892500
H	-9.13189200	-5.07175500	0.84880300

Int_2

SCF energy: -1929.665609

Free energy: -1928.058464

C	4.71002000	0.98840600	0.68017900
C	5.60751700	2.18545800	1.02106100
C	6.80828900	2.33140500	0.07163100
C	3.65980400	1.26419900	-0.41003100
C	6.45698200	2.71716400	-1.37145600

C	5.36677500	1.85830100	-2.00961100
H	5.32205900	0.14040900	0.35255300
H	5.00409100	3.10129900	1.02598400
H	7.35712400	1.37798500	0.06498900
H	6.10834600	3.75765100	-1.40277100
H	4.16230700	0.65500200	1.56598300
H	5.99079600	2.05626200	2.04074500
H	7.50230000	3.08020500	0.47479400
H	7.36115200	2.66577100	-1.99397200
H	5.26130300	2.10883800	-3.07061800
H	5.59274500	0.78714400	-1.94661100
O	3.23974500	0.07787400	-1.01306800
O	4.10270500	2.13969700	-1.41177500
Sn	1.87698600	-1.07149200	-0.07690900
C	2.45261400	-2.97239900	-0.86809200
C	1.71221300	-4.13479100	-0.60204200
C	3.61147700	-3.07430000	-1.65288900
C	2.12165100	-5.37177200	-1.10421200
H	0.80654900	-4.08483100	-0.00033900
C	4.01975000	-4.30990600	-2.15932100
H	4.19026200	-2.18020300	-1.86817600
C	3.27653000	-5.45921200	-1.88383000
H	1.54009800	-6.26457600	-0.89000500
H	4.91800800	-4.37682800	-2.76770700
H	3.59551100	-6.42099700	-2.27643800
C	2.00405100	-1.10334000	2.06144500
C	2.30016100	-2.31753400	2.69992700
C	1.74325900	0.03057900	2.84786700
C	2.33338700	-2.39937300	4.09391400
H	2.51054400	-3.20666600	2.10979800
C	1.77726500	-0.05173800	4.24096400
H	1.54092000	0.98505000	2.37230200
C	2.07019200	-1.26641900	4.86489400
H	2.56605700	-3.34495600	4.57647800
H	1.57720400	0.83282000	4.83979700
H	2.09535800	-1.32858700	5.94947300
C	-0.09063800	-0.45084200	-0.66290100
C	-1.11084400	-0.39036100	0.29826800
C	-0.38928400	-0.09491900	-1.98672200
C	-2.39811100	0.02813100	-0.04806000
H	-0.89922400	-0.64696100	1.33387900
C	-1.67423000	0.32417900	-2.33779000
H	0.38503400	-0.12960300	-2.74956000
C	-2.67755300	0.38922800	-1.36796000

H	-3.16939400	0.09863600	0.71259800
H	-1.89187200	0.60440700	-3.36513600
H	-3.66984200	0.73454900	-1.64196100
C	-3.07824200	4.40880500	-0.75190100
C	-1.98144900	3.73833400	0.10769400
C	-0.64652600	3.64129200	-0.63312900
C	-4.41385200	4.18092900	-0.10433700
C	0.43566200	2.96132000	0.21158600
C	1.67295100	2.63285700	-0.60816500
H	-2.89816800	5.48490800	-0.82882800
H	-1.86999400	4.30276000	1.04111900
H	-0.31292500	4.64101900	-0.94545600
H	0.71620400	3.59620400	1.06199600
H	-3.08090300	3.97136200	-1.75488300
H	-2.30434000	2.73027800	0.38695300
H	-0.80064000	3.05834300	-1.55064500
H	0.03430700	2.02992200	0.62375900
H	1.40459100	2.01661700	-1.47332800
H	2.16005500	3.54056600	-0.97927000
O	-4.94461800	4.84405800	0.73849100
O	2.57949600	1.91464600	0.23973400
O	-5.03196500	3.01430700	-0.61630500
C	-5.40063200	2.01238300	0.25115800
O	-4.93933100	1.90022800	1.35940500
C	-6.39735300	1.08149000	-0.39877100
H	-7.39020400	1.53092500	-0.24890400
H	-6.23051400	1.07803500	-1.48146200
C	-6.35618400	-0.33124800	0.18661600
H	-5.36617000	-0.76869800	0.00404000
H	-6.46887100	-0.26994300	1.27460800
C	-7.43368400	-1.24218500	-0.40687800
H	-7.32114400	-1.27767200	-1.50043900
H	-8.42500400	-0.80596500	-0.21517500
C	-7.37840900	-2.66329700	0.15971300
H	-6.39607500	-3.11050900	-0.03945900
H	-7.49760800	-2.63951000	1.25040700
C	-8.44996400	-3.57236800	-0.42447700
H	-8.33814100	-3.62048800	-1.52102200
H	-9.44795500	-3.15043200	-0.21706000
O	-8.30210000	-4.85813400	0.16469800
H	-8.98625400	-5.43706900	-0.20303500

Int_3

SCF energy: -1929.66978

Free energy: -1928.059218

C	3.52307400	-2.88226700	-1.79702100
C	2.84828800	-4.14217400	-2.35140600
C	1.94226700	-4.87400100	-1.35670300
C	2.62923000	-1.64683800	-1.62899300
C	0.85157400	-3.99952100	-0.72692600
C	1.39591300	-2.90073500	0.18749700
H	4.00897100	-3.07831800	-0.83345800
H	2.27431100	-3.86047000	-3.23957100
H	2.55726800	-5.29314200	-0.54637500
H	0.22222700	-3.54296400	-1.49948700
H	4.30896700	-2.55832200	-2.48555600
H	3.63151200	-4.83471600	-2.68528300
H	1.47446100	-5.72928200	-1.86116400
H	0.19874900	-4.63763200	-0.11646000
H	0.62575200	-2.58839000	0.89879500
H	2.24627000	-3.27271000	0.77481700
O	3.40221200	-0.52387800	-1.43876200
O	1.75994300	-1.68206400	-0.46508700
Sn	3.11063600	0.43538100	0.33013700
C	4.58794700	1.95344000	-0.01194900
C	4.75983200	3.01738200	0.88768200
C	5.40036600	1.90155000	-1.15550600
C	5.71993200	4.00426500	0.65443100
H	4.13863200	3.08916300	1.77876800
C	6.36216100	2.88676000	-1.38981800
H	5.27178400	1.08930400	-1.86536500
C	6.52317300	3.93812100	-0.48548100
H	5.84077000	4.82257800	1.35957000
H	6.98451400	2.83586900	-2.27964600
H	7.27122700	4.70490500	-0.66879800
C	1.21846000	1.41008600	0.57646800
C	1.12358400	2.78171500	0.29364900
C	0.07616600	0.74089400	1.04501100
C	-0.08259000	3.46507300	0.47031800
H	1.99496500	3.32386900	-0.06591400
C	-1.12825100	1.42268800	1.23294600
H	0.12095500	-0.32354400	1.25721300
C	-1.20800300	2.78795200	0.94286800
H	-0.14219300	4.52626900	0.24227400
H	-2.01154100	0.89660900	1.58473600
H	-2.15091700	3.30967500	1.07209200
C	3.57128700	-0.90871400	1.93165400

C	2.73652200	-0.99967700	3.05474200
C	4.66183300	-1.78612100	1.83134100
C	2.98145600	-1.94718000	4.05179100
H	1.88168400	-0.33459200	3.15479200
C	4.90690200	-2.73713800	2.82399100
H	5.32474100	-1.73683100	0.97035200
C	4.06473800	-2.81938100	3.93511000
H	2.32521600	-2.00694500	4.91613800
H	5.75337500	-3.41260300	2.73152300
H	4.25401500	-3.55945200	4.70789200
C	-3.30701500	1.95566700	-1.77407700
C	-2.52821700	0.62512700	-1.83177100
C	-1.15743700	0.77084300	-2.49481700
C	-4.31235200	1.95739000	-0.65694300
C	-0.35752000	-0.53205900	-2.42072300
C	1.06391100	-0.37122700	-2.95331100
H	-2.63468400	2.79849100	-1.59682500
H	-2.37495900	0.25625600	-0.81276400
H	-0.59914400	1.56015000	-1.97452800
H	-0.29734500	-0.85064000	-1.37729100
H	-3.82923000	2.13397100	-2.72316200
H	-3.13004100	-0.13001200	-2.35071700
H	-1.27176200	1.09804800	-3.53859400
H	-0.86786500	-1.33091600	-2.97608500
H	1.05214000	-0.17017900	-4.03051600
H	1.56390400	0.47228700	-2.46825500
O	-4.44961700	2.77822900	0.20623000
O	1.84624900	-1.55643100	-2.79139000
O	-5.15839500	0.83236800	-0.72219900
C	-5.25876700	0.01948700	0.38900600
O	-4.43914300	0.01168200	1.27264700
C	-6.49702000	-0.83524600	0.30587500
H	-6.51416100	-1.33758700	-0.66900700
H	-6.42477300	-1.59602700	1.08771200
C	-7.77806300	0.00347400	0.47306500
H	-7.73976400	0.53332800	1.43343300
H	-7.80861900	0.77128600	-0.30865400
C	-9.04325800	-0.85660200	0.40897100
H	-8.99832700	-1.62808400	1.19102600
H	-9.06795100	-1.39272200	-0.55095500
C	-10.32332200	-0.03265300	0.57149900
H	-10.31076600	0.49987600	1.53098600
H	-10.38174800	0.73317900	-0.21245700
C	-11.58282300	-0.88496700	0.50864200

H	-11.55316700	-1.64963000	1.30323600
H	-11.62180500	-1.41885600	-0.45605500
O	-12.70201700	-0.02230400	0.66527900
H	-13.50515900	-0.56287600	0.63031500

TS2

SCF energy: -1929.659017

Free energy: -1928.043108

C	4.38582900	-2.43919500	1.45644500
C	4.33730700	-2.82908100	2.93604200
C	3.68884200	-1.81330500	3.89226400
C	3.05188800	-2.23810200	0.74981500
C	2.16084300	-1.69473400	3.74998500
C	1.70891200	-0.69895900	2.68298700
H	4.96192100	-1.51966000	1.31328000
H	3.81699500	-3.78949100	3.03548400
H	4.15651400	-0.82683700	3.76489700
H	1.74575100	-2.68371700	3.53180500
H	4.90195600	-3.22638500	0.89136300
H	5.37106900	-3.00127600	3.26229800
H	3.91759500	-2.13143700	4.91700300
H	1.71814800	-1.36584800	4.69942800
H	0.64850400	-0.84822000	2.44469000
H	1.82840600	0.32634000	3.04674600
O	3.07407900	-1.80590500	-0.47200900
O	2.49432900	-0.79829500	1.49541500
Sn	2.66732100	0.40832500	-0.30798200
C	4.62524700	0.73396000	-1.14019900
C	5.15945200	2.03172800	-1.12364500
C	5.37806800	-0.29979000	-1.71802300
C	6.41507100	2.29308500	-1.67652500
H	4.59921300	2.84552800	-0.67027900
C	6.63418100	-0.03912700	-2.26907500
H	4.97940500	-1.30857100	-1.71815700
C	7.15366600	1.25698600	-2.25002100
H	6.81750900	3.30266100	-1.65585800
H	7.20994100	-0.84826500	-2.71159400
H	8.13199100	1.45824800	-2.67876800
C	0.95396500	0.23280200	-1.58781800
C	0.99130000	-0.62746000	-2.69672800
C	-0.21886900	0.96629000	-1.34714700
C	-0.10950400	-0.73748700	-3.54941400
H	1.87941800	-1.22333200	-2.88894600

C	-1.32498700	0.85489700	-2.19490200
H	-0.28506300	1.62130300	-0.48267500
C	-1.26785500	0.00361300	-3.30046800
H	-0.06469400	-1.40402000	-4.40721500
H	-2.23618300	1.40482300	-1.97897100
H	-2.13396600	-0.09059500	-3.94836100
C	2.43588500	2.22169400	0.87535900
C	1.72930600	3.33609900	0.39597700
C	3.13356200	2.36104600	2.08727100
C	1.69394800	4.53550400	1.11385300
H	1.20199800	3.28232500	-0.55321500
C	3.10267000	3.55487500	2.80988800
H	3.71896900	1.52872800	2.47206000
C	2.37580800	4.64465200	2.32577200
H	1.13638700	5.38344100	0.72429600
H	3.64856700	3.63754500	3.74642200
H	2.34947900	5.57566100	2.88563800
C	-3.45740200	-2.18236800	-1.57459800
C	-2.41541600	-2.00628600	-0.45377700
C	-1.23550000	-2.96957700	-0.60160500
C	-4.31991100	-0.96123800	-1.75516400
C	-0.12130800	-2.66719200	0.40387000
C	1.11310200	-3.52125800	0.14977600
H	-2.97066400	-2.36214600	-2.53623400
H	-2.02679700	-0.98455600	-0.48651600
H	-0.82869900	-2.86762400	-1.61567700
H	0.15555900	-1.61330800	0.31009500
H	-4.10534500	-3.04307400	-1.36183300
H	-2.89797900	-2.13118000	0.52244400
H	-1.57510700	-4.01035800	-0.49729800
H	-0.47379300	-2.82469200	1.43167200
H	0.88954700	-4.58243600	0.29690500
H	1.47775200	-3.36934900	-0.86865700
O	-4.54728300	-0.37879600	-2.77972800
O	2.18049300	-3.24677000	1.07172000
O	-4.89138600	-0.57343800	-0.53840300
C	-5.07598500	0.77304500	-0.25112300
O	-4.40086800	1.64619700	-0.72779900
C	-6.19370900	0.94262100	0.74499200
H	-6.00287700	0.28684600	1.60346200
H	-6.17283800	1.98006100	1.08926300
C	-7.56237100	0.59523600	0.12979000
H	-7.73207100	1.22469900	-0.75308700
H	-7.54477800	-0.44281000	-0.22231400

C	-8.70856800	0.78649900	1.12697900
H	-8.71425900	1.82817200	1.47847400
H	-8.52392200	0.16340300	2.01418700
C	-10.07348600	0.43751900	0.52776900
H	-10.26902900	1.05953500	-0.35495100
H	-10.08029800	-0.60525600	0.18548100
C	-11.21544800	0.62849100	1.51580900
H	-11.24026500	1.67770000	1.85553000
H	-11.04377800	0.00134100	2.40713100
O	-12.42471900	0.27048400	0.85952300
H	-13.15460100	0.39910600	1.48338900

Polymer chain with one-unit added

SCF energy: -1929.650108

Free energy: -1928.083378

C	-0.21917900	-1.94627000	-1.55862500
C	1.25744200	-1.94698300	-1.16762900
C	2.18166800	-2.00282400	-2.38973200
C	-1.14704000	-1.87737700	-0.36384100
C	3.67199200	-2.10660700	-2.04022800
C	4.22529700	-0.87983800	-1.32175300
H	-0.45336200	-1.09719400	-2.21518300
H	1.46353400	-1.05593200	-0.56503000
H	2.01301800	-1.11383700	-3.01573200
H	3.85074900	-2.98787300	-1.40988800
H	-0.47807300	-2.84218100	-2.13828500
H	1.45715700	-2.80358700	-0.51171000
H	1.90245600	-2.86627400	-3.00936700
H	4.26029500	-2.25104900	-2.95460600
H	4.03077000	0.02078400	-1.93063100
H	3.69787500	-0.73456700	-0.36457400
O	-0.80344600	-1.79162000	0.79571100
O	5.61690300	-1.06604800	-1.11344300
Sn	6.57884300	0.28910000	-0.00224100
C	8.63244400	-0.27904400	-0.06951000
C	9.36416800	-0.38810600	1.12275900
C	9.28872600	-0.51202400	-1.28849100
C	10.72037300	-0.71943100	1.09906200
H	8.87353300	-0.22194100	2.07953900
C	10.64467000	-0.84337900	-1.31394200
H	8.74139200	-0.44840900	-2.22603600
C	11.36136100	-0.94553400	-0.12000500
H	11.27519100	-0.80335100	2.02974300

H	11.14078800	-1.02508100	-2.26362100
H	12.41672300	-1.20351800	-0.14002600
C	6.26923100	2.25498200	-0.79704800
C	7.23447800	2.86435800	-1.61299500
C	5.08766000	2.95692300	-0.51061400
C	7.02306000	4.14198900	-2.13474400
H	8.16249200	2.34376600	-1.83960600
C	4.87341300	4.23451500	-1.03154000
H	4.33040900	2.51121800	0.13088300
C	5.84118500	4.82670900	-1.84519300
H	7.77917700	4.60387300	-2.76413400
H	3.95467500	4.76792800	-0.80211500
H	5.67622500	5.82151100	-2.25015900
C	5.69237400	0.17107900	1.94080400
C	5.68385800	1.27730900	2.80392600
C	5.08163400	-1.02041200	2.36236300
C	5.08955800	1.19196500	4.06498900
H	6.13296300	2.21775200	2.49112900
C	4.48201000	-1.10604300	3.61996100
H	5.06549600	-1.88339000	1.70055200
C	4.48869600	-0.00026600	4.47279200
H	5.09012400	2.05502100	4.72559400
H	4.00639600	-2.03154500	3.93309200
H	4.02156700	-0.06635600	5.45164000
C	-8.42427400	-1.83614200	1.14026200
C	-7.30635300	-1.89539100	0.08246700
C	-5.91161300	-1.85094200	0.71263400
C	-9.78930300	-1.90104800	0.50398200
C	-4.79384000	-1.91141200	-0.33348200
C	-3.41636700	-1.85901300	0.30515900
H	-8.34494300	-2.67479500	1.83717000
H	-7.41639200	-2.81418900	-0.50758700
H	-5.80265100	-2.68728100	1.41729300
H	-4.88120500	-2.83302600	-0.92263400
H	-8.34073000	-0.90126900	1.70781400
H	-7.42619400	-1.05726500	-0.61422600
H	-5.81091600	-0.93192700	1.30764700
H	-4.89396900	-1.07600500	-1.03813800
H	-3.26650600	-0.93572500	0.87549600
H	-3.25322700	-2.69756400	0.99099300
O	-10.57500400	-2.80473800	0.56971700
O	-2.44170600	-1.92131400	-0.75470200
O	-10.05296200	-0.71345500	-0.17997200
C	-10.89021800	-0.71455200	-1.29803700

O	-10.98338100	-1.65201700	-2.04018100
C	-11.58994000	0.61458700	-1.41895700
H	-10.84162100	1.41505100	-1.36652000
H	-12.06562000	0.64768800	-2.40285100
C	-12.62999700	0.81269400	-0.30012500
H	-13.35205200	-0.01330000	-0.32769200
H	-12.12643200	0.75824500	0.67224400
C	-13.36901200	2.14770500	-0.42793200
H	-13.86626800	2.19518400	-1.40728500
H	-12.63769400	2.96898800	-0.41405500
C	-14.40019400	2.35776800	0.68404800
H	-15.13760200	1.54508800	0.67415500
H	-13.90953700	2.32522800	1.66528100
C	-15.13937200	3.68231000	0.55795600
H	-15.65998600	3.72534600	-0.41361500
H	-14.41542200	4.51466300	0.57689300
O	-16.05783100	3.77424800	1.63932300
H	-16.53694200	4.61210400	1.55610600

TSA

SCF energy: -1391.600047

Free energy: -1390.375103

Sn	-0.93307600	-0.05348900	0.21441000
C	0.81857800	0.96599300	0.91831900
C	0.98347900	2.34459900	0.72565200
C	1.82863000	0.25256700	1.58253700
C	2.13276200	2.99673300	1.18024300
H	0.21429100	2.92241400	0.21846700
C	2.97013500	0.90346800	2.05217500
H	1.73279700	-0.82065200	1.71948500
C	3.12527400	2.27675800	1.84696500
H	2.25248500	4.06395100	1.01349900
H	3.74331300	0.33990700	2.56688400
H	4.01852200	2.78195600	2.20414700
C	-1.43081500	0.18116400	-2.06771800
C	-2.16617500	1.33418700	-2.43382100
C	-1.91620500	-1.07509600	-2.50571800
C	-3.31672800	1.24144000	-3.20626200
H	-1.81982500	2.31090900	-2.10632000
C	-3.08678200	-1.17732800	-3.25409400
H	-1.35033400	-1.96637400	-2.24731300
C	-3.78165700	-0.01746100	-3.60700500
H	-3.86288700	2.13664500	-3.48907900

H	-3.45377600	-2.14944600	-3.57045700
H	-4.69043400	-0.09204800	-4.19841100
C	-2.57687800	1.23503400	0.83562000
C	-3.87261000	1.05513500	0.32444000
C	-2.37985400	2.22682900	1.80758600
C	-4.93656300	1.84339900	0.76478500
H	-4.05948000	0.29389200	-0.42953600
C	-3.44096600	3.02432800	2.24793500
H	-1.38956000	2.38833600	2.22659000
C	-4.72045100	2.83373800	1.72652200
H	-5.93301800	1.68762600	0.35878200
H	-3.26716700	3.79272100	2.99706800
H	-5.54679200	3.45144800	2.06812300
C	-1.47733100	-1.98025500	0.98928100
C	-2.66971700	-2.07361800	1.72513700
C	-0.69328200	-3.13274900	0.81874700
C	-3.07296100	-3.29173300	2.27664400
H	-3.29166400	-1.19466700	1.87116600
C	-1.09846400	-4.34870700	1.37282300
H	0.22764900	-3.07196700	0.25115300
C	-2.28742200	-4.43126900	2.10032300
H	-3.99903200	-3.34928200	2.84280300
H	-0.48336000	-5.23451100	1.23582000
H	-2.59945000	-5.37991500	2.52933100
O	1.17518700	0.28998200	-2.41336000
H	-0.15462600	0.29564000	-2.17343600
C	1.63148800	-0.63510000	-1.65892600
O	0.89602900	-1.35938300	-0.92990300
C	3.13654400	-0.82826200	-1.62567900
H	3.37064600	-1.39396800	-0.72032000
H	3.42168200	-1.45669400	-2.48191800
C	3.89879500	0.50282500	-1.68662500
H	3.52883100	1.16534600	-0.89530100
H	3.65913900	0.99273000	-2.63563700
C	5.41854800	0.34450500	-1.54673300
H	5.89474800	1.30594100	-1.78506800
H	5.78593200	-0.37277100	-2.29600500
C	5.86510500	-0.09450800	-0.14789600
H	5.43636100	-1.07007400	0.11090800
H	5.49134300	0.61767600	0.59756600
C	7.37666000	-0.19037100	-0.01316000
H	7.83403400	0.78543000	-0.24940100
H	7.77067600	-0.91932200	-0.74137600
O	7.67485000	-0.58623900	1.32210500

H	8.63742300	-0.65877100	1.40397300
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TSB

SCF energy: -1391.583858

Free energy: -1390.362639

Sn	-1.32431700	-0.29937600	0.13398800
C	-0.57755600	-2.26319100	-0.35989600
C	-0.01268700	-3.06197600	0.64718000
C	-0.57774700	-2.74880700	-1.67561000
C	0.52672200	-4.31493500	0.34976600
H	0.01007500	-2.70443200	1.67456600
C	-0.03352400	-3.99939600	-1.97916400
H	-1.01576500	-2.15531700	-2.47517900
C	0.51881200	-4.78398000	-0.96581700
H	0.95417700	-4.92425800	1.14193000
H	-0.04090500	-4.36041000	-3.00442100
H	0.94085900	-5.75771500	-1.19942200
C	-0.69523600	2.05651200	-0.56306400
C	-1.29607900	3.02602700	0.26428300
C	-0.65762100	2.31573800	-1.94782800
C	-1.83348000	4.20227700	-0.26283200
H	-1.34456600	2.85306100	1.33748900
C	-1.19063000	3.48639700	-2.48575000
H	-0.20579500	1.58732800	-2.61917100
C	-1.78153100	4.43061700	-1.64045800
H	-2.29347600	4.93734900	0.39260400
H	-1.15266700	3.66587300	-3.55704900
H	-2.20172700	5.34273800	-2.05609900
C	-1.83579500	-0.01986600	2.18988900
C	-0.84306900	0.14387400	3.16822500
C	-3.18456900	-0.00045800	2.57675000
C	-1.19481100	0.31207200	4.50929400
H	0.20122500	0.15514200	2.86949500
C	-3.53530900	0.16631400	3.91797800
H	-3.96720800	-0.11149900	1.82946300
C	-2.53983300	0.32127300	4.88477400
H	-0.42014600	0.44012000	5.26104300
H	-4.58270300	0.17878800	4.20806600
H	-2.81211700	0.45306900	5.92864100
C	-3.12700800	-0.16197300	-1.07458100
C	-3.76911200	1.05065600	-1.36349000
C	-3.73751700	-1.35829900	-1.48510000
C	-4.98418000	1.06761700	-2.05061200

H	-3.32669100	1.99087300	-1.05400800
C	-4.95255400	-1.34291700	-2.17566000
H	-3.26596300	-2.31394600	-1.27154900
C	-5.57626300	-0.12844200	-2.46165900
H	-5.46798800	2.01666500	-2.26720800
H	-5.40861300	-2.27836800	-2.48969900
H	-6.52030100	-0.11338700	-2.99994400
O	0.84237800	0.30774300	0.51556100
H	0.30877300	1.28940500	-0.00961900
C	1.96199400	-0.22606800	-0.17176500
H	2.00648500	-1.30619800	0.01385300
H	1.84436800	-0.09778500	-1.26231900
C	3.24836000	0.44663300	0.29613600
H	3.17245900	1.52731600	0.11545100
H	3.33258300	0.31692500	1.38295900
C	4.49226700	-0.11315200	-0.39996500
H	4.38936900	0.00862000	-1.48849500
H	4.55474000	-1.19657300	-0.22042000
C	5.78674800	0.55751700	0.06732600
H	5.73387000	1.63832500	-0.11063200
H	5.90023600	0.43760600	1.15141500
C	7.02178800	-0.00689200	-0.63234800
H	6.95164600	0.11190800	-1.72190600
H	7.11599700	-1.08796700	-0.46288500
C	8.30767100	0.64500000	-0.17829700
O	8.41084100	1.52064200	0.65213500
O	9.38375800	0.12613400	-0.82409400
H	10.16029800	0.60038900	-0.47136800

TSC

SCF energy: -1006.426633

Free energy: -1005.505172

Sn	0.33337700	0.17630700	-0.25056900
C	2.24670400	-0.82423600	-0.26852300
C	3.37569200	-0.18692000	-0.80902200
C	2.38861000	-2.12779600	0.22949500
C	4.61517100	-0.82804500	-0.83700300
H	3.28845500	0.81993700	-1.21149100
C	3.62543600	-2.77702100	0.19294400
H	1.53154200	-2.64114100	0.65759800
C	4.74022100	-2.12657300	-0.33762300
H	5.48189900	-0.31763900	-1.24897200
H	3.71821900	-3.78908600	0.57843200

H	5.70333200	-2.62919300	-0.36334400
C	-1.43478500	-0.41260200	-1.90335700
C	-2.57427500	0.41214900	-1.80702000
C	-1.64045100	-1.79570300	-2.08197700
C	-3.86316400	-0.11657700	-1.89315800
H	-2.44460000	1.48358900	-1.66732100
C	-2.92298200	-2.33440800	-2.16770000
H	-0.78124600	-2.46043000	-2.15735600
C	-4.03530600	-1.49170700	-2.07402600
H	-4.73029300	0.53430700	-1.81910600
H	-3.06256700	-3.40322700	-2.30578700
H	-5.03688100	-1.90841100	-2.14007200
C	0.15687400	2.23815200	0.29818700
C	0.53646800	3.26612200	-0.57833200
C	-0.35017700	2.57216400	1.56370200
C	0.42011500	4.60233000	-0.18977100
H	0.90828200	3.00995400	-1.56576600
C	-0.46302900	3.90861000	1.95189300
H	-0.66071800	1.78818100	2.25024900
C	-0.07718500	4.92417800	1.07490500
H	0.71434500	5.39340300	-0.87489000
H	-0.85468900	4.15728300	2.93485600
H	-0.16724700	5.96485000	1.37535000
C	-0.71910100	-0.90224500	1.33231300
C	-2.08177400	-1.22606100	1.30197800
C	0.00763900	-1.19230100	2.49985200
C	-2.69921900	-1.83050400	2.39935600
H	-2.67481500	-1.00654900	0.42158500
C	-0.60677200	-1.79532300	3.60082300
H	1.06847100	-0.95679500	2.55804900
C	-1.96319700	-2.11806300	3.55017500
H	-3.75723300	-2.07672600	2.35537200
H	-0.02611400	-2.01387400	4.49348800
H	-2.44433600	-2.58918200	4.40321900
O	0.78683600	0.79602700	-2.40277200
H	-0.32123800	0.16630900	-2.40708500
H	1.49481600	0.26513700	-2.80504400

A

SCF energy: -1159.369476

Free energy: -1158.395459

Sn	-1.23399800	0.10590300	-0.01396800
C	-0.53695500	-1.74886700	0.79174100

C	-1.23614700	-2.93679700	0.52837400
C	0.61133600	-1.80188800	1.59795400
C	-0.79352900	-4.15235900	1.05406100
H	-2.13246500	-2.91670700	-0.08710900
C	1.05464800	-3.01640400	2.12353200
H	1.16590100	-0.89319400	1.81941200
C	0.35253500	-4.19222100	1.85006900
H	-1.34086700	-5.06662500	0.84160400
H	1.94555800	-3.04607000	2.74495000
H	0.69777500	-5.13819800	2.25797200
C	-0.56092800	1.72398800	1.21075100
C	-0.19300400	2.94508800	0.62470500
C	-0.45013100	1.57648000	2.60161600
C	0.27385000	3.99684800	1.41477500
H	-0.26032300	3.07474000	-0.45259600
C	0.01453400	2.62960900	3.39235800
H	-0.71683900	0.63505300	3.07713100
C	0.37648000	3.83985700	2.79855900
H	0.55911100	4.93700400	0.95084500
H	0.09754500	2.50443600	4.46858500
H	0.74029200	4.65888800	3.41275300
C	-3.27557000	-0.05140400	-0.59288500
C	-3.68814400	0.44643500	-1.83847000
C	-4.22024000	-0.66196300	0.24629800
C	-5.02333100	0.33872900	-2.23186700
H	-2.96168000	0.90340800	-2.50458100
C	-5.55501600	-0.76876900	-0.14872800
H	-3.92090500	-1.06778500	1.21064300
C	-5.95651000	-0.26628000	-1.38774000
H	-5.33424700	0.72382700	-3.19916200
H	-6.27897600	-1.24438300	0.50739800
H	-6.99506900	-0.34915700	-1.69619700
O	-0.45651400	0.57873000	-1.83671800
C	0.82866200	0.66344500	-2.22014500
O	1.12670000	1.08597100	-3.31654800
C	1.86484900	0.19649000	-1.20227500
H	1.74461500	0.79720900	-0.28852700
H	1.62838000	-0.83682800	-0.91480200
C	3.30329600	0.29121500	-1.70348900
H	3.51601500	1.32639000	-1.99471300
H	3.40494000	-0.30472000	-2.61798700
C	4.31277400	-0.17972100	-0.65281600
H	4.07842800	-1.21427900	-0.36023800
H	4.19937200	0.42667200	0.25858100

C	5.76144000	-0.10118300	-1.14143800
H	6.00843700	0.92999900	-1.42463000
H	5.88865900	-0.71311600	-2.04355500
C	6.76193300	-0.56840200	-0.09469100
H	6.54024400	-1.61098300	0.19070000
H	6.66050000	0.04661800	0.81583700
O	8.06751400	-0.45418200	-0.64851200
H	8.70293700	-0.75303100	0.01883900

B

SCF energy: -1159.371103

Free energy: -1158.393184

Sn	-1.43717600	-0.08267200	-0.10592500
C	-1.95062000	0.82045200	1.76704600
C	-2.60185300	0.07542000	2.76250000
C	-1.64076000	2.16518200	2.02456200
C	-2.93490800	0.65951500	3.98610300
H	-2.85659100	-0.96655900	2.58225500
C	-1.97117200	2.75092800	3.24815100
H	-1.14531900	2.76556700	1.26474700
C	-2.61831200	1.99747300	4.22942500
H	-3.44034400	0.07263500	4.74848000
H	-1.72578100	3.79292500	3.43581600
H	-2.87695600	2.45265100	5.18164600
C	-1.40693500	1.44012700	-1.61363100
C	-0.46140700	1.36895300	-2.64834100
C	-2.29331700	2.52686400	-1.58068600
C	-0.40754100	2.35880400	-3.63124500
H	0.24100900	0.53929600	-2.68074000
C	-2.24246000	3.51701500	-2.56444100
H	-3.02476400	2.61273300	-0.77983300
C	-1.29967200	3.43238700	-3.59050900
H	0.32986000	2.29447300	-4.42706400
H	-2.93473300	4.35411800	-2.52901600
H	-1.25859200	4.20285700	-4.35567100
C	-2.57886800	-1.85564300	-0.41974900
C	-1.93213400	-3.02294000	-0.85434400
C	-3.96113500	-1.89256800	-0.18263300
C	-2.65608100	-4.20000300	-1.05339400
H	-0.85876400	-3.01148600	-1.02431600
C	-4.68517500	-3.06998700	-0.38084700
H	-4.48302200	-1.00428100	0.16787000
C	-4.03228200	-4.22367800	-0.81849800

H	-2.14633900	-5.09949500	-1.38835300
H	-5.75545900	-3.08764600	-0.19294600
H	-4.59482000	-5.14040100	-0.97347100
C	1.50124000	-0.00080600	0.25078500
H	1.43338700	0.24079300	1.32560600
H	1.49899400	0.96201300	-0.29055900
C	2.81064000	-0.72979100	-0.02704900
H	2.79069900	-1.69197200	0.50083500
H	2.85791000	-0.96200600	-1.09929400
C	4.04254100	0.07728000	0.39157700
H	3.98052100	0.31066400	1.46479400
H	4.04175200	1.04578300	-0.13042400
C	5.35694000	-0.65357100	0.10469200
H	5.36816900	-1.62035800	0.62217700
H	5.43095200	-0.88525800	-0.96459400
C	6.58009400	0.15742000	0.52853800
H	6.60826500	1.13027100	0.01935000
H	6.55096700	0.39129700	1.60117900
C	7.88587000	-0.54877300	0.24469900
O	0.41999100	-0.82313800	-0.15312200
O	8.01324400	-1.63648500	-0.27271500
O	8.95059500	0.19327900	0.64547000
H	9.74102400	-0.33462500	0.42443100

C

SCF energy: -774.216351

Free energy: -773.539987

Sn	0.02614500	-0.04257100	0.66226200
C	0.16235900	2.00305800	0.03287900
C	1.40968500	2.57721700	-0.25784300
C	-0.99140500	2.78967400	-0.10966100
C	1.50325900	3.90700900	-0.67196000
H	2.31567600	1.98133100	-0.17007900
C	-0.90100400	4.11975200	-0.52531300
H	-1.97096100	2.36163400	0.09291500
C	0.34729200	4.67919600	-0.80425700
H	2.47491600	4.33978600	-0.89494800
H	-1.80192200	4.71801600	-0.63339800
H	0.41900500	5.71388100	-1.12843200
C	1.68640400	-1.17979800	-0.04655200
C	2.95034600	-1.07103900	0.55397800
C	1.53819500	-2.02070600	-1.15985200
C	4.04076200	-1.78253200	0.04964400

H	3.08572900	-0.44179700	1.43036100
C	2.62731500	-2.73314800	-1.66551400
H	0.56454100	-2.13115000	-1.63289300
C	3.88003100	-2.61220400	-1.06172500
H	5.01371800	-1.69323400	0.52562800
H	2.49850400	-3.38357200	-2.52662600
H	4.72865600	-3.16615700	-1.45394000
C	-1.85923600	-0.83343600	0.02943100
C	-2.54825400	-1.76106000	0.82591800
C	-2.42221900	-0.44772300	-1.19738800
C	-3.76712700	-2.29485200	0.40369000
H	-2.13412600	-2.06281500	1.78515900
C	-3.64077000	-0.98194200	-1.62254800
H	-1.91575100	0.28198200	-1.82594100
C	-4.31284300	-1.90696600	-0.82190000
H	-4.29205800	-3.01164700	1.02971100
H	-4.06598900	-0.67521000	-2.57459800
H	-5.26133600	-2.32289900	-1.15087400
O	0.14193700	-0.20073800	2.65088800
H	-0.31809300	0.52331300	3.10160500

D

SCF energy: -1544.539403

Free energy: -1543.235666

C	4.13846100	0.21432000	-0.19176300
C	4.25233900	0.15332500	1.34735300
C	5.15056600	1.24673500	1.93395800
C	3.14906700	1.25439300	-0.66475100
C	4.69525500	2.67695500	1.61777400
C	4.64235500	3.00986600	0.12973700
H	5.12557900	0.41474200	-0.63022500
H	3.25200600	0.21584300	1.78648300
H	6.17712100	1.10691400	1.56113000
H	3.70460200	2.86097800	2.04513400
H	3.78746200	-0.73888300	-0.58417700
H	4.66199900	-0.82969700	1.60683800
H	5.19551400	1.12467300	3.02277600
H	5.39452000	3.38446000	2.08308300
H	4.60846000	4.09068500	-0.02042800
H	5.51668400	2.62132900	-0.40838600
O	2.07810800	0.96460400	-1.17394700
O	3.43484800	2.55778800	-0.52568800
Sn	-0.14389700	-0.74218900	-0.25013300

C	-1.06437300	0.29854000	-1.89164900
C	-2.28569500	-0.22716000	-2.34844900
C	-0.56010000	1.45762100	-2.50236300
C	-2.99505600	0.39879700	-3.37607600
H	-2.69912000	-1.12585400	-1.89978800
C	-1.27535000	2.08568900	-3.52397300
H	0.39440200	1.85954600	-2.18436000
C	-2.49404300	1.56274400	-3.95955700
H	-3.93719000	-0.02251000	-3.71675100
H	-0.87615000	2.98681100	-3.98190800
H	-3.04770400	2.05676200	-4.75348700
C	1.45911100	-2.09984300	-0.59576800
C	1.90566500	-2.38643600	-1.89295300
C	2.12444900	-2.68060900	0.49450900
C	2.99540200	-3.23458100	-2.09823400
H	1.41909100	-1.92737900	-2.75008300
C	3.21592800	-3.52843900	0.29146900
H	1.81387500	-2.45064300	1.51053200
C	3.65304800	-3.80441700	-1.00544800
H	3.33710200	-3.44441900	-3.10831800
H	3.72842000	-3.96602400	1.14407400
H	4.50455000	-4.46037700	-1.16468100
C	-1.75933800	-1.77203500	0.73151600
C	-1.56023600	-3.00778700	1.36571000
C	-3.04294700	-1.20535900	0.77317100
C	-2.61119400	-3.64743600	2.02796700
H	-0.58204100	-3.48266500	1.34204900
C	-4.09794900	-1.83514100	1.43545400
H	-3.23146200	-0.26051800	0.27642100
C	-3.87818000	-3.06086100	2.06709800
H	-2.44099800	-4.60405200	2.51520000
H	-5.07537900	-1.35940700	1.45863200
H	-4.69186900	-3.55940400	2.58695100
O	0.65237200	0.33735800	1.29975200
C	0.70541800	1.63646700	1.59457600
O	1.58686500	2.07599800	2.31369300
C	-0.41531000	2.50444300	1.04429200
H	-0.16874900	3.55063200	1.24005000
H	-0.45666100	2.37344700	-0.04246900
C	-1.77686500	2.12457500	1.65964000
H	-1.80146600	1.04369500	1.83860400
H	-1.87699100	2.59375600	2.64631200
C	-2.97158100	2.48521600	0.77110400
H	-2.82514900	2.00775400	-0.20809400

H	-2.99395300	3.56587800	0.57715900
C	-4.30107700	2.01596700	1.38207900
H	-4.14513800	1.07147400	1.91560200
H	-4.66535900	2.73269700	2.12765200
C	-5.38302000	1.77163400	0.33953800
H	-4.97553500	1.14762000	-0.47341000
H	-5.70501100	2.72362100	-0.11314000
O	-6.47063200	1.11248400	0.98565500
H	-7.17162000	0.97900500	0.33020300

TS_S1

SCF energy: -1544.507619

Free energy: -1543.207554

C	1.96345800	2.65728300	-1.15023200
C	1.72590900	3.88567000	-0.26404200
C	0.93694600	5.02070300	-0.91613300
C	0.78507200	1.76312000	-1.52245500
C	-0.43665500	4.59566500	-1.44212700
C	-0.36975500	3.62149900	-2.61611600
H	2.42420100	2.94930200	-2.10690300
H	1.22017600	3.55322600	0.64500300
H	1.51514200	5.44367900	-1.75141900
H	-1.04846300	4.17364900	-0.63714200
H	2.67865300	2.00167000	-0.64987300
H	2.71056000	4.26456200	0.03558100
H	0.80943200	5.82987600	-0.18716800
H	-0.97149600	5.48266900	-1.80619300
H	-1.31121100	3.62241100	-3.16871900
H	0.42870600	3.91439900	-3.31032100
O	1.03846400	0.50620300	-1.74318400
O	-0.20102700	2.22430500	-2.29760900
Sn	1.12366000	-0.67913600	0.00839600
C	1.99199000	-2.30858900	-1.09445900
C	1.80009600	-3.62777200	-0.65431700
C	2.79391900	-2.08994700	-2.22529000
C	2.39654300	-4.70030300	-1.32152200
H	1.16953800	-3.82810700	0.20974600
C	3.39208100	-3.15942300	-2.89449000
H	2.93734600	-1.07846100	-2.59545600
C	3.19518300	-4.46578000	-2.44184600
H	2.23608000	-5.71624300	-0.96990900
H	4.00795500	-2.97544300	-3.77117400
H	3.66006500	-5.29850900	-2.96297700

C	2.56226500	0.07930800	1.39673000
C	3.83976500	-0.50164400	1.41554600
C	2.26116100	1.10006100	2.31390600
C	4.80466500	-0.06655500	2.32707900
H	4.08759300	-1.29597600	0.71493600
C	3.22553500	1.52754700	3.22821700
H	1.28249700	1.56968800	2.30009400
C	4.49677500	0.94831100	3.23409100
H	5.79294300	-0.51877800	2.32895300
H	2.98463100	2.31682600	3.93551500
H	5.24554800	1.28718600	3.94522000
C	-0.70157700	-1.44046400	0.82481100
C	-1.06606700	-1.14499000	2.14742000
C	-1.53253700	-2.27664100	0.06372100
C	-2.23437500	-1.67712100	2.69717500
H	-0.44781100	-0.48774700	2.75238100
C	-2.71066500	-2.79414700	0.60652200
H	-1.25990000	-2.53343400	-0.95733800
C	-3.05989800	-2.49759600	1.92584400
H	-2.50597600	-1.44067100	3.72209300
H	-3.35221000	-3.43172300	0.00415700
H	-3.97386600	-2.90368700	2.35026300
O	0.09082100	1.56618700	0.20923000
C	-1.16073500	1.78930700	0.62732000
O	-1.37453100	2.25100600	1.73679200
C	-2.28339700	1.39349800	-0.32205000
H	-2.48368600	2.23924200	-0.99379200
H	-1.93043800	0.58288500	-0.96545200
C	-3.55949500	0.98544700	0.41683900
H	-3.29828900	0.27236800	1.20320900
H	-3.98576800	1.85797800	0.92509700
C	-4.59284900	0.34517600	-0.51245500
H	-4.11861400	-0.49197000	-1.04437900
H	-4.90535900	1.06491100	-1.28402900
C	-5.81829300	-0.17204100	0.24504300
H	-5.49912800	-0.88619000	1.01455400
H	-6.32045400	0.65198700	0.76809600
C	-6.82585000	-0.85995300	-0.66285900
H	-6.33578800	-1.69597400	-1.19087200
H	-7.17921100	-0.15251400	-1.43206600
O	-7.90494400	-1.32480900	0.14152800
H	-8.55194300	-1.74720000	-0.44283200

E

SCF energy: -1544.517997

Free energy: -1543.209934

C	2.16900000	2.30275100	-1.06208700
C	2.47212000	3.62497600	-0.34618400
C	1.99309200	4.88516400	-1.07153600
C	0.69698600	1.84438500	-1.10655500
C	0.51398200	4.85977700	-1.47253800
C	0.18800700	3.79450500	-2.52323200
H	2.53253300	2.30835700	-2.09701000
H	2.03079800	3.57900200	0.65363700
H	2.59167000	5.02998900	-1.98324300
H	-0.12884100	4.71538500	-0.59608200
H	2.71660800	1.51105400	-0.54464000
H	3.55841000	3.69007800	-0.20634500
H	2.18532700	5.75865700	-0.43592100
H	0.24803400	5.83425300	-1.90292700
H	-0.72077000	4.06883100	-3.06623400
H	1.00384500	3.73949500	-3.25934200
O	0.58640100	0.50630600	-1.37416800
O	-0.11114900	2.48373900	-2.04197900
Sn	0.98590300	-0.89555000	0.04982400
C	1.90339200	-2.34992800	-1.21497700
C	2.35007300	-3.58244000	-0.71303500
C	2.08270900	-2.06825800	-2.57821800
C	2.96370700	-4.51330600	-1.55351000
H	2.22300100	-3.82746400	0.33975700
C	2.69251400	-3.00082400	-3.41990800
H	1.74175400	-1.11670600	-2.97682000
C	3.13418600	-4.22237500	-2.90834400
H	3.30632800	-5.46364900	-1.15291300
H	2.82462500	-2.77388100	-4.47457300
H	3.61040000	-4.94674800	-3.56358400
C	2.34064200	-0.20383600	1.55311600
C	3.62925600	-0.76009400	1.58612800
C	1.98638200	0.75944500	2.51335900
C	4.55108800	-0.36209900	2.55687000
H	3.92188600	-1.50483700	0.84911600
C	2.91084800	1.15287600	3.48279200
H	1.00482600	1.22343500	2.49952800
C	4.19107500	0.59521900	3.50599900
H	5.54706900	-0.79675800	2.57000900
H	2.62993700	1.90060600	4.21957800
H	4.90680300	0.90731600	4.26185200

C	-0.90503900	-1.50885000	0.83430100
C	-1.20868100	-1.33988000	2.19312300
C	-1.85209700	-2.12215900	-0.00165100
C	-2.43356800	-1.77316400	2.70530500
H	-0.49721700	-0.85711100	2.85706500
C	-3.07783700	-2.55199100	0.50845200
H	-1.63830800	-2.26667700	-1.05830000
C	-3.36808600	-2.37901700	1.86392900
H	-2.66095400	-1.62931200	3.75772500
H	-3.80667300	-3.01899800	-0.14833800
H	-4.32282400	-2.71241500	2.26090000
O	0.20528000	2.11676400	0.26044100
C	-1.07571200	1.93807000	0.70009200
O	-1.25688200	2.03501700	1.89614400
C	-2.17509100	1.62412700	-0.29021100
H	-2.34159900	2.51423400	-0.90808600
H	-1.80833200	0.86334100	-0.98481600
C	-3.45961900	1.17249600	0.40290600
H	-3.22110400	0.38580300	1.12333000
H	-3.87861100	2.00178400	0.98521500
C	-4.49452300	0.64797700	-0.59472500
H	-4.04212400	-0.16766700	-1.17646400
H	-4.75439200	1.43510700	-1.31813000
C	-5.76200400	0.13518000	0.09289100
H	-5.49509800	-0.62654200	0.83553900
H	-6.25558800	0.94902600	0.63939800
C	-6.75739100	-0.47170900	-0.88347400
H	-6.27547400	-1.29716300	-1.43551500
H	-7.05910400	0.28395500	-1.62827300
O	-7.87946000	-0.93895000	-0.14181200
H	-8.52198300	-1.30140300	-0.76974400

F

SCF energy: -1544.517922

Free energy: -1543.211909

C	-2.83272100	2.02232500	-1.50782200
C	-3.42417000	3.42226500	-1.30680800
C	-3.89174000	3.73311400	0.11846200
C	-1.47280300	1.74008600	-0.84948600
C	-2.83265700	3.50786900	1.20555400
C	-2.49248700	2.03555500	1.43090600
H	-3.52308000	1.23992400	-1.16848100
H	-2.67700500	4.15829000	-1.61686000

H	-4.76840800	3.11305600	0.35910100
H	-1.91877000	4.07140300	0.98870700
H	-2.66675200	1.85411400	-2.57629100
H	-4.27896500	3.52969900	-1.98661200
H	-4.23235900	4.77521400	0.15838300
H	-3.22276100	3.88764200	2.15911500
H	-2.04144600	1.89058100	2.41580100
H	-3.41173800	1.43300400	1.39294400
O	-0.87580600	0.64823300	-1.41398100
O	-1.52657200	1.45385200	0.54291600
Sn	-0.59577500	-0.97678900	-0.19436600
C	1.15386700	-1.68150200	-1.21723800
C	1.99825900	-2.63375800	-0.62625100
C	1.54151200	-1.10251300	-2.43638500
C	3.20776800	-2.98897300	-1.22840900
H	1.72723200	-3.09498600	0.32084600
C	2.75009800	-1.45560800	-3.03961200
H	0.90534300	-0.35540400	-2.90227700
C	3.58730400	-2.39505700	-2.43349100
H	3.85434700	-3.72334900	-0.75541900
H	3.04248900	-0.99267700	-3.97821500
H	4.53110500	-2.66422400	-2.89966900
C	-0.08592700	-0.88321500	1.88983700
C	1.25205600	-0.89188600	2.30791600
C	-1.09367400	-0.81137500	2.86447400
C	1.57803100	-0.81652000	3.66447300
H	2.05001000	-0.95475600	1.57475100
C	-0.77167000	-0.74221000	4.22102100
H	-2.13960000	-0.81040700	2.56787700
C	0.56633500	-0.73996200	4.62219100
H	2.62060800	-0.81626800	3.97135500
H	-1.56260800	-0.68858500	4.96453800
H	0.81790300	-0.68144300	5.67752900
C	-2.47160300	-1.97642900	-0.41236600
C	-2.91432900	-2.90103000	0.54571200
C	-3.29017100	-1.70480300	-1.51968500
C	-4.14858400	-3.53892200	0.40218800
H	-2.30096000	-3.12464400	1.41569900
C	-4.52438300	-2.34087900	-1.66376500
H	-2.96389900	-0.98881300	-2.26879300
C	-4.95450400	-3.25778300	-0.70223000
H	-4.48138800	-4.25193500	1.15177900
H	-5.15039300	-2.12155800	-2.52461600
H	-5.91545900	-3.75247100	-0.81395600

O	-0.71028500	2.94766400	-1.05223500
C	0.60006500	3.15898900	-0.70779700
O	1.01226000	4.29263200	-0.78342600
C	1.45421400	1.98301300	-0.29430900
H	1.06144300	1.59242300	0.65326600
H	1.30983400	1.19431300	-1.03342900
C	2.94168800	2.31224400	-0.17964000
H	3.28655400	2.73704900	-1.13009500
H	3.10592000	3.08734500	0.57724700
C	3.74933000	1.05205600	0.15094700
H	3.46205000	0.24920300	-0.54206700
H	3.47305200	0.70244000	1.15566400
C	5.26407700	1.25208100	0.08173600
H	5.55157300	1.60583900	-0.91668600
H	5.58586100	2.02234900	0.79431500
C	6.02081300	-0.03556800	0.37348200
H	5.70837500	-0.81433200	-0.34261500
H	5.75824400	-0.39871100	1.38228600
O	7.41506900	0.23171500	0.27157900
H	7.89110600	-0.59227600	0.45271300

TS_S2

SCF energy: -1544.506452

Free energy: -1543.196922

C	-2.59795200	2.81602700	-0.30757900
C	-2.90737700	3.74874600	0.86503700
C	-2.84247400	3.12614600	2.26799600
C	-1.17357400	2.30754900	-0.43425900
C	-1.43250600	2.73916300	2.74770500
C	-0.99134900	1.34103200	2.33250600
H	-3.25013200	1.93801800	-0.29776600
H	-2.23397500	4.61283200	0.82169000
H	-3.50026400	2.24632300	2.31503800
H	-0.70731300	3.48158300	2.39594500
H	-2.79105100	3.34639500	-1.24972300
H	-3.92113700	4.13885000	0.70936200
H	-3.25991700	3.85776300	2.97080500
H	-1.39678600	2.75956100	3.84491600
H	0.03727600	1.15162500	2.66713900
H	-1.63429800	0.59133700	2.80812600
O	-0.87776100	1.46154500	-1.34587300
O	-1.06929600	1.15487700	0.92007600
Sn	-0.84261500	-0.60825200	-0.29286900

C	1.03717000	-0.98110700	-1.27445800
C	1.72872000	-2.16807100	-0.98103000
C	1.58094300	-0.10348200	-2.22457200
C	2.94845700	-2.45679400	-1.59820500
H	1.32524700	-2.87276300	-0.25873900
C	2.79981600	-0.39198100	-2.84174900
H	1.05659400	0.81442300	-2.46669500
C	3.49035400	-1.56331800	-2.52362500
H	3.47455500	-3.37646900	-1.35600100
H	3.21402000	0.30284700	-3.56742000
H	4.44461600	-1.77972600	-2.99559600
C	-0.71290800	-1.75646500	1.55099400
C	0.52083000	-1.91083000	2.20484300
C	-1.86511900	-2.22219500	2.20534300
C	0.60556300	-2.52613100	3.45590900
H	1.43326000	-1.54490700	1.73926200
C	-1.78732200	-2.84058400	3.45588500
H	-2.84126900	-2.09764200	1.74271700
C	-0.54984500	-2.99568000	4.08258800
H	1.57148600	-2.63608400	3.94243300
H	-2.69191200	-3.19679400	3.94220900
H	-0.48703800	-3.47494700	5.05580300
C	-2.65912100	-1.17479900	-1.27677700
C	-3.21216200	-2.44150600	-1.02793700
C	-3.28936100	-0.33549900	-2.20826200
C	-4.37731700	-2.85253600	-1.67921300
H	-2.73533600	-3.11985700	-0.32507300
C	-4.45639200	-0.74455300	-2.85630200
H	-2.85579000	0.63381500	-2.43022800
C	-5.00398700	-2.00097600	-2.58996900
H	-4.79379700	-3.83558900	-1.47596400
H	-4.93620900	-0.08382600	-3.57363100
H	-5.91193000	-2.31818500	-3.09582400
O	-0.27933600	3.32543800	-0.16871200
C	1.07543500	3.17596500	-0.51542500
O	1.53307600	3.86807500	-1.38032100
C	1.84133500	2.21998300	0.35951500
H	1.77532200	2.59579200	1.39021600
H	1.30415700	1.27011100	0.36653000
C	3.28975600	2.01046800	-0.07996000
H	3.31518200	1.90705000	-1.16868200
H	3.88876500	2.89739400	0.15933700
C	3.89566600	0.75709500	0.55696300
H	3.24475800	-0.09663400	0.32860100

H	3.90586800	0.86042600	1.65245800
C	5.30637400	0.45425900	0.04829300
H	5.29543500	0.39350800	-1.04662700
H	5.99809600	1.26276000	0.31770700
C	5.84693500	-0.85919500	0.59162700
H	5.16202600	-1.67647200	0.31189400
H	5.88243500	-0.82183200	1.69388500
O	7.14452800	-1.06535100	0.04282400
H	7.48858500	-1.89916200	0.39607000

G (Active catalyst)

SCF energy: -1544.504292

Free energy: -1543.222839

Sn	-2.82982000	0.20331500	0.07731500
C	-4.03016900	1.17282300	-1.40332100
C	-3.67783600	2.42722200	-1.92352200
C	-5.17575400	0.52989900	-1.89632300
C	-4.46152900	3.03413600	-2.90704700
H	-2.78207700	2.93549000	-1.57192200
C	-5.95989600	1.13595400	-2.87966000
H	-5.44436400	-0.45330500	-1.51835300
C	-5.60459300	2.38904300	-3.38309000
H	-4.17975100	4.00605600	-3.30348300
H	-6.84517100	0.63010500	-3.25594900
H	-6.21491800	2.86037700	-4.14871800
C	-3.14333100	0.61108800	2.14835100
C	-2.75774300	1.82581300	2.73488800
C	-3.71155800	-0.38561900	2.95659900
C	-2.94326900	2.04459900	4.10125300
H	-2.30471200	2.61027800	2.13180000
C	-3.89926200	-0.16569400	4.32251400
H	-3.99762200	-1.33599500	2.51363200
C	-3.51630100	1.04887900	4.89471700
H	-2.64008200	2.98855100	4.54623700
H	-4.34030000	-0.94285000	4.94105900
H	-3.66063600	1.21853500	5.95826000
C	-0.76041400	0.43550100	-0.44459500
C	0.23418300	0.43328700	0.54610900
C	-0.37037200	0.46127000	-1.79230100
C	1.58760800	0.44132700	0.20196100
H	-0.04615300	0.40973300	1.59696900
C	0.98194800	0.47072000	-2.14180200
H	-1.12331400	0.47540200	-2.57739500

C	1.95898500	0.45526400	-1.14486200
H	2.34728800	0.41269400	0.97705200
H	1.27289300	0.48692300	-3.18886100
H	3.00943300	0.45966100	-1.41973500
C	2.34605700	-4.14735600	-0.95224700
C	1.20019900	-3.52685400	-0.12251500
C	-0.15122300	-3.58893300	-0.83926800
C	3.65429000	-3.81426200	-0.29368600
C	-1.26888600	-2.97562900	0.01227100
C	-2.51897100	-2.59639100	-0.78979200
H	2.24046800	-5.23472900	-1.00120000
H	1.14796600	-4.03893500	0.84585900
H	-0.39274200	-4.62522900	-1.11344200
H	-1.54605800	-3.64299100	0.83763900
H	2.33268900	-3.73663300	-1.96690300
H	1.43571900	-2.47743600	0.08950100
H	-0.06808000	-3.02674100	-1.78033000
H	-0.87740000	-2.06295200	0.47410100
H	-2.20119500	-2.15042700	-1.74894500
H	-3.09760600	-3.49571500	-1.04280200
O	4.24339000	-4.45224400	0.53110000
O	-3.37828200	-1.72483900	-0.07325300
O	4.15003100	-2.58162600	-0.76649200
C	4.55437500	-1.62067800	0.13559300
O	4.14499400	-1.56767200	1.26681000
C	5.51810400	-0.65640800	-0.51366200
H	6.49165400	-1.16632700	-0.55884500
H	5.21617700	-0.50706400	-1.55690500
C	5.63751400	0.66756800	0.24073200
H	4.65778900	1.16183600	0.26567100
H	5.89937800	0.46206900	1.28451700
C	6.66806500	1.60881600	-0.38814700
H	6.40305600	1.79118100	-1.44010200
H	7.65098100	1.11556100	-0.40184500
C	6.77294400	2.94469800	0.35209700
H	5.79880300	3.45044800	0.35696600
H	7.04349500	2.77414700	1.40187900
C	7.80004500	3.88207400	-0.26623600
H	7.53872200	4.07534300	-1.32061000
H	8.79272700	3.40092600	-0.25971700
O	7.80606400	5.08547200	0.49123000
H	8.46509200	5.68059500	0.10396600

TS_insertion

SCF energy: -1315.144122

Free energy: -1313.924975

C	2.82256600	-1.91898000	-1.26738000
C	3.87245300	-2.38498000	-0.25401200
C	5.04789900	-1.40586800	-0.07700100
C	1.86679300	-0.81003300	-0.80702200
C	4.72345800	-0.10960100	0.67851800
C	3.53096000	0.65822100	0.12171600
H	3.32018300	-1.50462700	-2.15551800
H	3.39307700	-2.58687200	0.71174300
H	5.44080200	-1.15361700	-1.07307100
H	4.50632600	-0.34014900	1.73003100
H	2.22137500	-2.75853400	-1.62400400
H	4.27766600	-3.34278100	-0.60405000
H	5.86212900	-1.91910500	0.45047400
H	5.60476300	0.54661100	0.67339000
H	3.38256700	1.60397900	0.65127800
H	3.64358900	0.89092300	-0.94371100
O	1.27286900	-0.14131600	-1.71482700
O	2.32938100	-0.09763100	0.33340000
Sn	-0.50783800	0.40187700	-0.14534600
C	-1.82430000	0.18119100	-1.83096100
C	-1.36260400	0.06109200	-3.15115300
C	-3.20760200	0.17272600	-1.59234400
C	-2.26818900	-0.05897000	-4.20755900
H	-0.29517600	0.04280300	-3.34157600
C	-4.11201100	0.05551900	-2.65040000
H	-3.58590500	0.25461100	-0.57639700
C	-3.64252700	-0.06039000	-3.95954300
H	-1.90054700	-0.15310200	-5.22640300
H	-5.18081600	0.05147400	-2.45203000
H	-4.34497600	-0.15390200	-4.78373900
C	-1.85192500	0.25601700	1.56966000
C	-2.36515500	1.42624100	2.15262400
C	-2.33208000	-0.97842400	2.03221600
C	-3.31321700	1.36563300	3.17815200
H	-2.02629300	2.40085000	1.80927000
C	-3.28020900	-1.04471900	3.05497000
H	-1.97110600	-1.90273000	1.59188600
C	-3.76927000	0.12837400	3.63366300
H	-3.69415200	2.28334300	3.61933600
H	-3.63866200	-2.01149200	3.39997500
H	-4.50539400	0.07794700	4.43167000

C	0.50680200	2.27423200	0.12763100
C	0.72088500	2.79995000	1.40921700
C	1.03231000	2.95857200	-0.97730300
C	1.43694500	3.98763100	1.58403900
H	0.33534200	2.28083400	2.28289300
C	1.73911500	4.15007300	-0.80707100
H	0.91265700	2.54569200	-1.97479700
C	1.94391600	4.66624100	0.47482800
H	1.60010000	4.38015600	2.58458500
H	2.13730800	4.67263100	-1.67316200
H	2.49947100	5.59074100	0.60821500
C	0.46229700	-1.74676400	0.19414300
C	-0.25528000	-2.67045300	-0.60070200
C	0.80434200	-2.13950200	1.50667000
C	-0.63423100	-3.91496300	-0.10472500
H	-0.50290100	-2.39691600	-1.62400600
C	0.44320200	-3.38855700	2.00652100
H	1.37285900	-1.45023500	2.12284700
C	-0.27796300	-4.27539900	1.20025100
H	-1.19424600	-4.60780900	-0.72677100
H	0.71842100	-3.67618100	3.01760000
H	-0.55882700	-5.25149100	1.58688200

TS_S3

SCF energy: -1701.781606

Free energy: -1700.244957

C	-5.06240200	1.06351800	-0.77881700
C	-4.28883800	0.86443800	-2.09596700
C	-2.79763600	1.14761800	-1.90688400
C	-4.63503300	0.05988400	0.27310700
C	-1.89642100	0.59261100	-3.00827700
C	-0.42640500	0.67565900	-2.62113500
H	-4.88323200	2.06148300	-0.36996000
H	-4.43866700	-0.16649200	-2.43699600
H	-2.46985300	0.70740700	-0.96054800
H	-2.14393400	-0.45749000	-3.20789800
H	-6.13857900	0.94138300	-0.94973300
H	-4.71372000	1.51933400	-2.86653000
H	-2.63392400	2.22631200	-1.79402100
H	-2.04256100	1.13709300	-3.95147400
H	0.21930700	0.24600700	-3.39029100
H	-0.13480700	1.71159100	-2.43146400
O	-4.10427300	0.32943000	1.33343300

O	-0.19247700	-0.06511600	-1.40359500
Sn	0.98224500	0.75473100	0.28467500
C	-0.26512700	2.53134800	0.20899400
C	0.12252300	3.62772100	-0.57832700
C	-1.48197000	2.61242400	0.90356500
C	-0.69110700	4.75768200	-0.69328800
H	1.07405800	3.60801600	-1.10606000
C	-2.29734600	3.74098700	0.79568500
H	-1.82310600	1.79345900	1.52719400
C	-1.90731200	4.81277400	-0.00954400
H	-0.37595100	5.59325200	-1.31314800
H	-3.23819000	3.77580700	1.33876100
H	-2.54296000	5.68992300	-0.09800600
C	0.41807800	-0.33274300	2.04612200
C	-0.92501700	-0.66144500	2.29745800
C	1.39265100	-0.75294800	2.96394200
C	-1.28104300	-1.39062200	3.43339700
H	-1.71279200	-0.35910500	1.61441300
C	1.03875600	-1.48607200	4.09938900
H	2.43988000	-0.51003700	2.79765200
C	-0.29901800	-1.80730700	4.33433200
H	-2.32697100	-1.62363500	3.61453600
H	1.80651100	-1.80564600	4.79909300
H	-0.57524500	-2.37549000	5.21842400
C	2.95952800	1.59130800	0.15501600
C	3.24619600	2.74442300	0.90368700
C	3.96436500	1.05122500	-0.66111800
C	4.51396600	3.32810500	0.85935200
H	2.47490700	3.20309900	1.51900700
C	5.22992500	1.63914700	-0.71381600
H	3.74718300	0.17548500	-1.26358900
C	5.50785000	2.77385800	0.05055700
H	4.72372200	4.21647400	1.44933200
H	5.99812200	1.21359100	-1.35436000
H	6.49380000	3.22925100	0.01116200
C	-0.38536100	-2.47372400	-0.70860000
C	-1.90500200	-2.46786800	-0.90952200
C	-2.55714500	-3.51507700	0.00128800
C	0.38359900	-1.56723600	-1.65774000
C	-4.09071600	-3.49086800	0.06246700
C	-4.68973600	-2.28834700	0.78940800
H	-0.17566400	-2.21260000	0.32898200
H	-2.29081400	-1.47192300	-0.67836500
H	-2.16861800	-3.38658200	1.02202400

H	-4.52581000	-3.54790600	-0.94339300
H	0.00543900	-3.48416900	-0.87790300
H	-2.15433200	-2.66969100	-1.95864400
H	-2.23332600	-4.51360800	-0.32186700
H	-4.42699500	-4.38949100	0.59593900
H	-5.67285400	-2.53524000	1.20442800
H	-4.04873300	-1.93909000	1.60190700
O	0.63459400	-1.82868000	-2.81146300
O	-4.91103400	-1.19876400	-0.13541600
O	1.76830900	-1.07753500	-0.73019000
C	2.57884500	-2.07195800	-0.11814000
H	1.97999900	-2.69032900	0.56624400
H	3.32383400	-1.54853100	0.49675800
C	3.28067100	-2.94223900	-1.15614500
H	3.88178700	-2.29576000	-1.80907800
H	2.53088700	-3.41131600	-1.80333900
C	4.16744800	-4.01029600	-0.50917600
H	3.55458700	-4.64516500	0.14650000
H	4.90864500	-3.52561100	0.14236400
C	4.88594000	-4.88448100	-1.54024300
H	5.53123800	-4.27846300	-2.18751000
H	5.51220600	-5.64322200	-1.05753400
H	4.16608800	-5.40259800	-2.18506900

TS_S4

SCF energy: -1239.892566

Free energy: -1238.835431

C	-3.44299900	1.14941900	1.52872600
C	-2.30522800	2.16935100	1.60032700
C	-1.61896500	2.28304600	2.96329100
C	-3.11780400	-0.33867800	1.49728700
C	-1.02446300	0.97194500	3.48527100
C	-2.04973600	-0.14057900	3.70008300
H	-4.13805200	1.28815600	2.37022300
H	-1.57780200	1.93011100	0.82112900
H	-2.34751000	2.65071700	3.70083900
H	-0.23306300	0.60758800	2.81989300
H	-4.02672800	1.32592100	0.62610900
H	-2.72298700	3.14931600	1.33893000
H	-0.82833200	3.04167500	2.90823300
H	-0.54879800	1.16033600	4.45708600
H	-1.63620900	-0.90870300	4.35765000
H	-2.95255600	0.25820300	4.18149800

O	-4.05968900	-1.09729200	1.02163900
O	-2.43101800	-0.89291000	2.53630600
Sn	-3.30156400	-2.06380300	-0.77480200
C	2.86402600	0.79707900	-0.37100500
C	1.85187100	-0.28151500	0.02309900
C	0.40155400	0.19552600	-0.10267900
C	-0.59391400	-0.86784600	0.35133000
H	2.73751800	1.68186400	0.26324700
H	2.04275000	-0.60189400	1.05864200
H	0.26716800	1.10644800	0.49280400
H	2.67355700	1.13568500	-1.39600000
H	1.99887400	-1.17430000	-0.60227200
H	0.18176400	0.46823800	-1.14264800
H	-0.39786100	-1.80269900	-0.19986900
H	-0.45731600	-1.10750100	1.41350500
O	-1.94385100	-0.48152000	0.13227200
O	-4.25806200	-0.91342900	-2.11375000
C	-4.68655700	0.42394300	-1.96542400
H	-5.47297000	0.61093400	-2.71261400
H	-5.14890300	0.58375700	-0.97807200
C	-3.54291400	1.42148700	-2.16711200
H	-2.74144300	1.17509800	-1.46061600
H	-3.12776900	1.27719200	-3.17364900
C	-3.97079400	2.87986300	-1.97953600
H	-4.43673300	3.00000200	-0.99029100
H	-4.74953100	3.13464200	-2.71179200
C	-2.80075400	3.85904300	-2.10793100
H	-3.12434200	4.89720400	-1.97052800
H	-2.02919300	3.64526700	-1.35802700
H	-2.32989900	3.78262900	-3.09537600
C	4.30855600	0.31004900	-0.26557100
H	4.47031300	-0.55726100	-0.92005300
H	4.51949500	-0.04830500	0.75195500
C	5.31040200	1.39823500	-0.61969000
O	6.63184400	1.08046700	-0.59389200
O	4.99179500	2.52547200	-0.91602800
C	7.08588500	-0.23956900	-0.25985200
H	6.73261100	-0.52053100	0.74062200
H	6.68758500	-0.96864400	-0.97728900
C	8.60563800	-0.22456900	-0.30369800
H	8.92522800	0.09363400	-1.30378600
H	8.97028000	0.53444700	0.39958800
C	9.21003900	-1.59169800	0.03402500
H	8.82831300	-2.34481200	-0.66948300

H	8.87256800	-1.90514500	1.03192700
C	10.74027300	-1.58201300	-0.00828500
H	11.15173900	-2.56735400	0.23570800
H	11.10448800	-1.30299600	-1.00405500
H	11.14910600	-0.86020500	0.70862400

TS_S5

SCF energy: -1239.908548

Free energy: -1238.834635

C	-4.46003300	-1.99957100	-1.41420200
C	-3.11929400	-2.69298000	-1.68311100
C	-2.00272900	-1.71153200	-2.04841600
C	-4.43765200	-1.04845100	-0.23257900
C	-0.62898000	-2.38098600	-2.10272200
C	0.51895600	-1.38958300	-2.24035400
H	-4.79698500	-1.42062300	-2.27916000
H	-2.82813500	-3.25605600	-0.78970200
H	-1.96417900	-0.90389000	-1.30836800
H	-0.46461300	-2.96244500	-1.18771200
H	-5.23359900	-2.75148100	-1.20629900
H	-3.25189000	-3.42515900	-2.49005100
H	-2.22704400	-1.23349600	-3.01316900
H	-0.58167400	-3.09203200	-2.93959500
H	1.47312600	-1.92848000	-2.29170000
H	0.41099300	-0.79472300	-3.15846800
O	-4.99018300	0.03182300	-0.20478300
O	0.54082900	-0.48754500	-1.13095100
Sn	1.56930200	1.44273300	-1.36469800
C	0.73315800	-0.71226600	1.43725600
C	-0.63889300	-1.38409200	1.55948100
C	-1.32545900	-0.96115000	2.86320500
C	1.51684800	-1.16136500	0.23536000
C	-2.78363100	-1.41598100	3.01960000
C	-3.75868100	-0.78708100	2.02976600
H	0.61744800	0.37196400	1.39751400
H	-1.24740600	-1.08918300	0.70283900
H	-1.29544600	0.13516400	2.93821200
H	-2.86298700	-2.50822900	2.94768200
H	1.36415000	-0.95690000	2.30214700
H	-0.54174900	-2.47673900	1.52141400
H	-0.74420500	-1.33924800	3.71521000
H	-3.12255600	-1.14545200	4.02795500
H	-4.78292500	-0.78524600	2.41718700

H	-3.49084400	0.24620400	1.79503500
O	1.99017000	-2.22562400	-0.03496100
O	-3.75332500	-1.56541900	0.81001100
O	2.66032500	0.17508500	0.04960000
C	3.99440000	-0.28029000	-0.18340200
H	3.95724200	-1.23001200	-0.73218700
H	4.50512200	0.45796900	-0.81652300
C	4.73200800	-0.46153300	1.13662000
H	4.70574100	0.48545100	1.69132900
H	4.18518900	-1.19843500	1.73897500
C	6.17955500	-0.92387800	0.94223400
H	6.18707700	-1.86316100	0.37219600
H	6.71918300	-0.18829100	0.32881300
C	6.91851500	-1.12392600	2.26795400
H	6.41794400	-1.87876200	2.88611100
H	7.95048600	-1.45426600	2.10556800
H	6.95126400	-0.19197400	2.84512000
O	0.58791100	2.19558000	0.23467000
C	-0.43681400	3.16513600	0.16419100
H	-0.57405600	3.56499500	-0.85799300
H	-0.15755100	4.02425800	0.79457800
C	-1.76668800	2.59480900	0.65870800
H	-1.61129100	2.21211000	1.67704500
H	-2.04041800	1.72972100	0.03851600
C	-2.89853100	3.62778900	0.65624500
H	-3.09502700	3.94735400	-0.37687100
H	-2.56631400	4.52666900	1.19548100
C	-4.19297000	3.10304900	1.28416600
H	-4.03060800	2.82948500	2.33506900
H	-4.98258800	3.86308100	1.26037200
H	-4.56029500	2.21528000	0.75963700

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ARTICLE

Effective Regulation of Polycaprolactone Molecular Weight and Oligomers Content Using Tetraphenyltin Catalyst

Caihong Gong^{ac}, Jinxia Li^b, Chunwang Yi^{*ac}, Shuanglin Qu^{*b}

There is a lack of effective approaches that produce polycaprolactone materials (PCL) with a high molecular weight, narrow polymer dispersity index (PDI), and fewer formation of oligomers. The immigration of the remained oligomers predominantly causes poor PCL quality and induces odor release. This limits the extensive application of PCL materials. This study investigates the effects of different catalysts and loadings on the PCL performance along with the formation of oligomers in detail. The oligomers were successfully separated using gel permeation chromatography (GPC). This was followed by a quantitative and qualitative identification using high-resolution mass spectrometry (HRMS) and low field nuclear magnetic (L-field NMR) analysis. The results show that tetraphenyltin is an effective catalyst to promote the reaction and produce high-performance PCL that possesses the highest Mn (65000), narrowest PDI (1.37), and the lowest content of oligomers (7.466 wt.%). Density functional theory (DFT) studies that were combined with characterizing key intermediates verified that an anhydride bond was formed close to the end hydroxyl group in the PCL chain because of the special catalytic mechanism. This unusual chemical structure successfully inhibited the chain from being broken by the “back-biting” behavior, which is helpful for lowering the content of oligomers. This study can provide a scalable synthetic approach to creating high-performance polymers.

1. Introduction

The main paragraph text follows directly on here. Polycaprolactone (PCL) has various biological applications, such as being a controlled drug release carrier,^[1-4] fluorescent probe,^[5] cell-encapsulation device,^[6] tissue culture bed frame,^[7-11] biological dye,^[12] and medical modeling material.^[8, 13-16] This is because of its excellent biodegradation^[17-19] and biocompatibility.^[20-22] Several studies have reported that minimal water, oxygen, and hydroxy compounds can initiate the ring-opening polymerization of caprolactone.^[23] However, this can only produce low molecular weight PCL in the absence of a catalyst. Similarly, most catalysts such as diisopropyl amino lithium,^[24] stannous octoate,^[25] and organic acid tin [Sn (OTf)₂]^[26] insignificantly influence synthesis during caprolactone polymerization. These catalysts can only be used to prepare PCL with a molecular weight (Mn) varying from 4000 to 15200. Furthermore, most of the prepared PCLs have a wide polymer dispersity index (PDI) owing to the generation of

oligomers, or the simultaneous polymerization and degradation during polymerization. Although phosphazene bases can generate PCL with a high Mn (≈ 38000), the conversion rate was only 14% when reacting with caprolactone for more than 10 days at 80 °C.^[27] Methylaluminoxane-trimethylaluminum is a rare catalyst that can increase the Mn of PCL to 223800.^[28] However, the “back-biting” side reaction is competitive with the caprolactone polymerization process. This generates cyclic oligomers and makes the PCL similar to polyamide 6 (PA6),^[29] which contains certain quantities of oligomers. The authors did not investigate the mechanic performance of the prepared PCL and the negative effects of cyclic oligomers on the PCL properties further.

The solubility in organic solvents and the melting point of oligomers were close to PCL. This made the substances difficult to separate. Generally, the remaining oligomers can damage the material performance and release unpleasant odors after migrating progressively to the surface of the materials. This limits the application and development of PCL significantly.^[30] Recent developments in technology include gel permeation chromatography (GPC) and mass spectrum (MS) technologies. These approaches have been used to identify and determine the oligomers.^[31-32] However, an effective method to suppress the formation of oligomers have not been proposed. Therefore, significant challenges exist in PCL performance improvement, especially for the regulation of the content of

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oligomers, molecular weight, and PDI of the PCL. Therefore, a new technology using a tetraphenyltin (Ph_4Sn) catalyst to prepare high-performing PCL is reported in this study. The molecular weight and the mechanical properties of PCL and the oligomer content could be conveniently regulated through varying tetraphenyltin loadings. Furthermore, characterization of key reaction intermediates and density functional theory (DFT) studies revealed the detailed reaction mechanism and verified that the catalyst can effectively suppress the formation of oligomers.

2. Experiment

2.1 Polymerization

The polymerization tests were performed using a "one-pot" method. Caprolactone and catalyst were added to a four-neck round bottle in a fixed mass ratio. Polymerization followed at 200 °C for 10 h in nitrogen air according to the synthetic approach shown in Fig. 1(a). Catalysts with different steric hindrance, such as tetraphenyltin, triphenyltin chloride, dimethyldiphenyltin, and tetramethyltin, were selected to synthesize the PCL. The main influencing factors of the polymerization process were investigated. These include the effects of different reaction times (2 – 14 h), temperature (100 – 240 °C), and catalyst dosage (0.1 – 5% by weight) on the polymerization process. Other reactions were avoided using nitrogen protection that was used in the experiment. After synthesized, the products were pulverized into fine particles and dried to a constant weight at 40 °C in vacuum conditions for further analysis. All reaction process parameters are listed in Table S1.

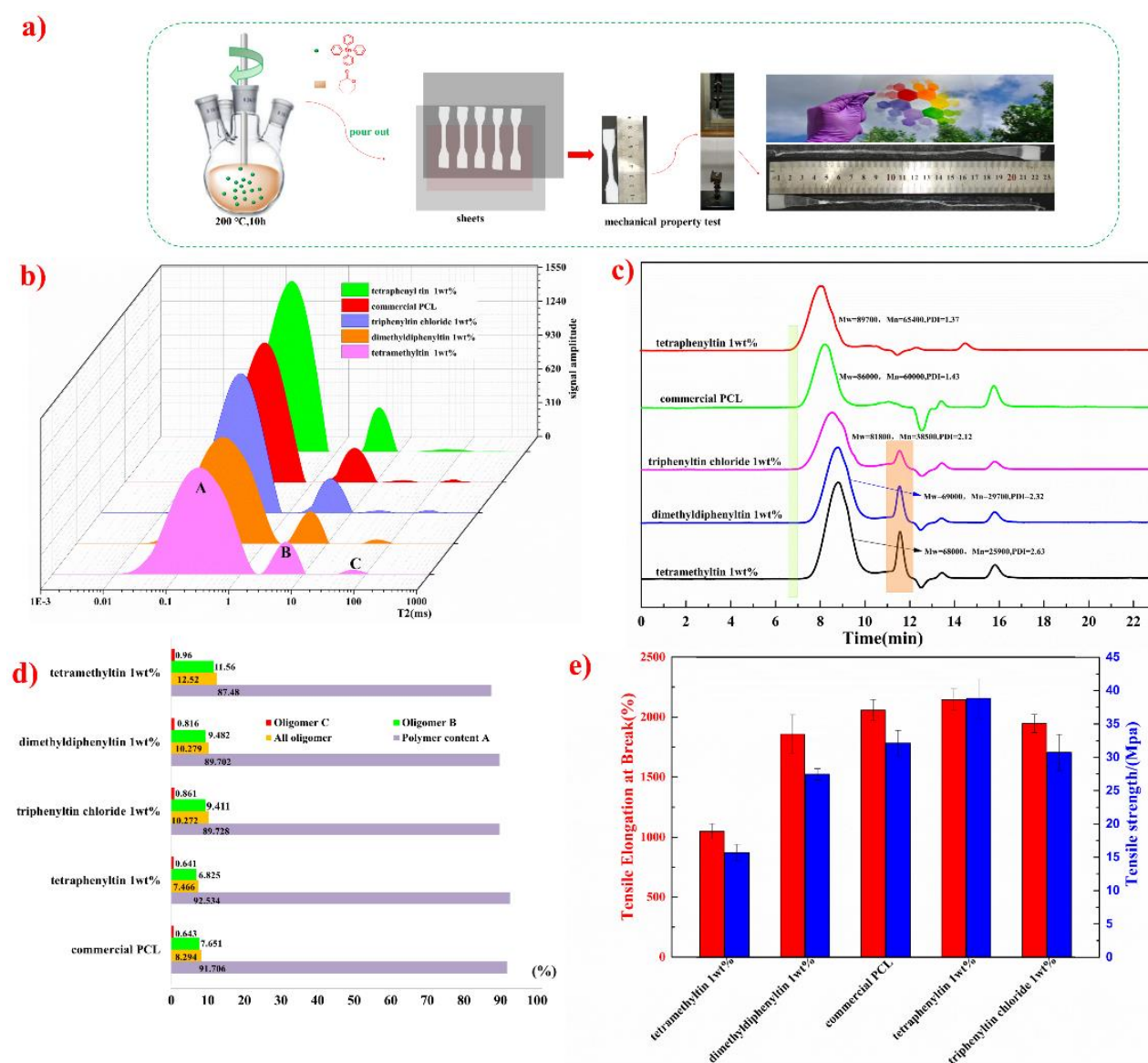


Figure 1. a) Synthesis route, Dumb-bell samples before and after tensile strength test (tetraphenyltin catalyst). b) Low field NMR patterns: "A" means long chain segment, "B" and "C" means small molecular chain segment. c) GPC curves. d) High-resolution mass spectrogram of oligomers. e) Mechanical properties.

3. Results and discussion

The conclusions section should come in this section at the end of the article, before the acknowledgements. The PCL properties were obtained using a 1 wt.% catalyst mass ratio under the same reaction conditions (200 °C, 10 h). These are displayed in Fig. 1 and Table S2. The GPC results (Fig. 1(c)) show that the tetraphenyltin system produces PCL with the highest M_n (65000) and the narrowest PDI (1.37). Additionally, small peaks appeared during the retention time of 11–16 min. This demonstrated that a certain number of oligomers with a molecular weight of less than 2000 was produced during the PCL synthesis.^[33] The content of polymers and oligomers in the PCL was measured further using low field nuclear magnetic (L-field NMR) analysis.^[34] This indicated that the tetraphenyltin catalyzed PCL has the lowest oligomers content (7.466 wt.%, Fig. 1(b)), which is comparable to that of the current commercial PCL. However, the PCL resulted from tetraphenyltin catalyst is vastly superior to other lab-prepared PCLs that were produced by using the other three catalysts

and most reported catalysts.^[23, 25] Furthermore, the results indicate that the oligomers content greatly influences the properties of the PCL. Higher content of oligomers leads to worse mechanical properties. Notably, the strain–stress tests show that the elongation and tensile strength of the tetraphenyltin catalyzed PCL reached 2000% and 38.5 MPa, respectively (Fig. 1(a, e)). This is also significantly better than current commercial (and the other lab-prepared) products. Especially, compared to the reported products with best elongation of 900%, the elongation is remarkably increased []. Besides, the tetraphenyltin catalyzed PCL was stable without peculiar smell after exposed to natural condition for half a year. However, the other lab-prepared PCLs released odor after only being kept for days, owing to the immigration of the remained oligomers. Therefore, tetraphenyltin is the best catalyst for producing PCL polymer that has optimum properties. The optimum process conditions for the PCL preparation were investigated further. A 1 wt.% dosage of tetraphenyltin was maintained for 10 h at 200 °C (Fig. 1, Table S2, and Table S3).

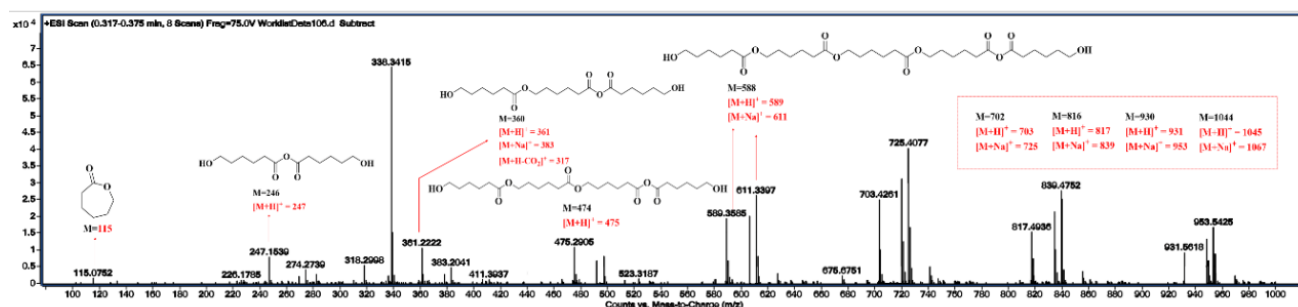
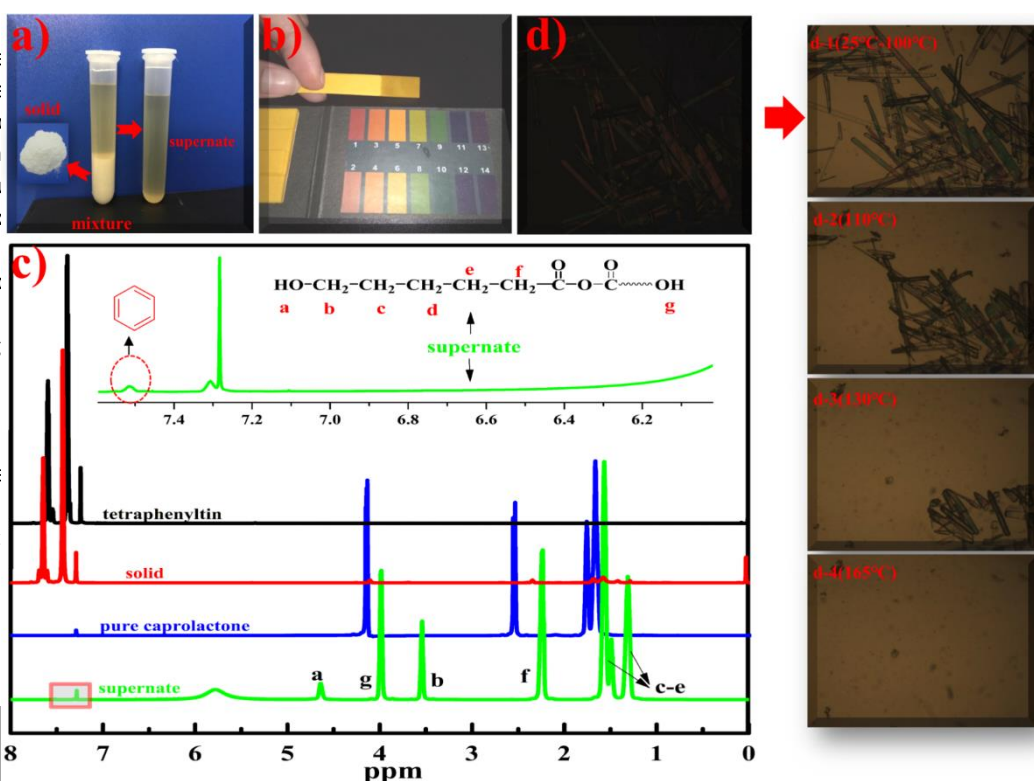


Figure 2. High-resolution mass spectrogram of oligomers.

The components related to small peaks from the GPC analysis (Fig. 1(c)) were collected. Fig. 2 is the pattern of the high-resolution (HRMS) that shows that there is a caprolactone in the components. Previously, it was reported that the active end groups (i.e., hydroxyl) can attack the ester or amide bonds in the polymer chain through "back-biting". This results in cyclic oligomers as shown in Fig. S1.^[23, 29] However, the cyclic oligomers and other typical cyclic oligomers of Fig. 2 are not observed in the mass spectra. Additionally, ionic fragment peaks that correspond to the linear oligomers with the regularity of the mass spectra. Possible chemical structures are shown in Fig. S2. A new anhydride bond (CO–O–CO) via a different catalytic mechanism was involved in the synthesis.



been proved through DFT calculations and will be discussed in detail in the following sections. The HRMS result shows that the “back-biting” behavior of the end hydroxyl groups has been effectively restricted, thereby significantly reducing the generation of cyclic oligomers.^[35]

A well-designed experiment was performed to study the possible mechanism for the formation of PCL. White intermediates were generated after the caprolactone, and tetraphenyltin reacted at 120 °C for 10 h in a four-neck round

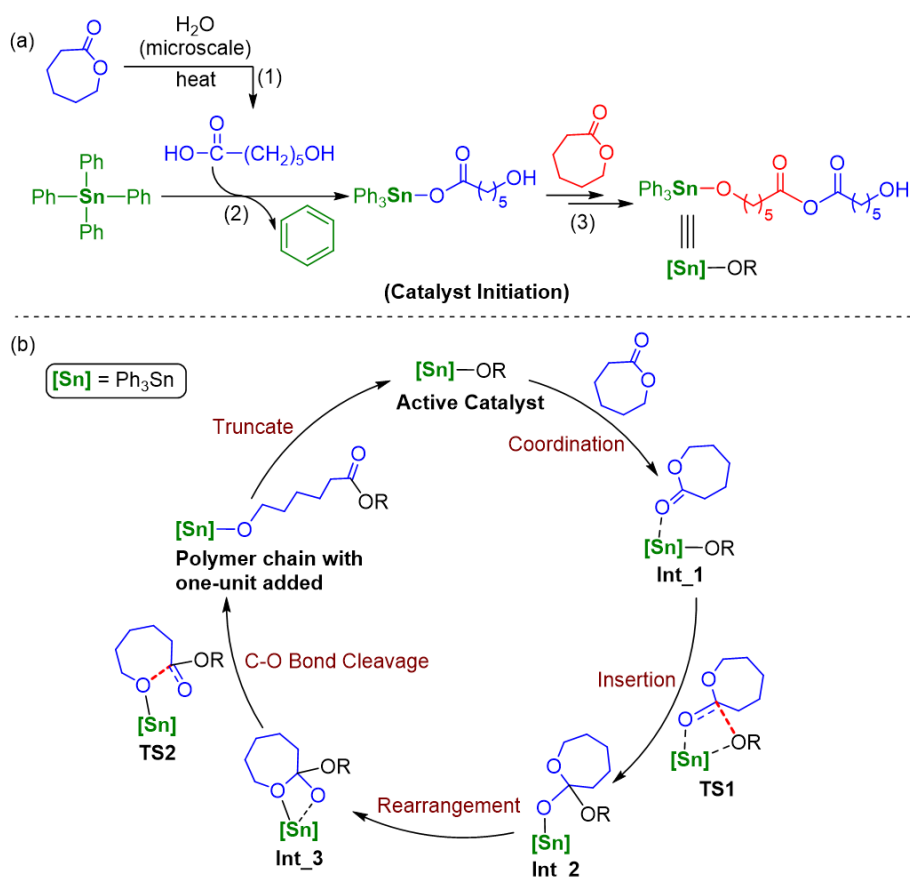
Figure 3. a) Intermediate product. b) pH test of supernate. c) Proton nuclear magnetic resonance (¹H-NMR) spectra of the bottom solid, supernate, pure caprolactone, and tetraphenyltin. d) Polarizing heat table microscope (POM) image of the separated bottom solid. (d 1 – 4) Melting behaviors of intermediates under POM at different temperatures.

The intermediates refract colorful light under polarized optical microscopy (Fig. 3(d)), which indicates that the intermediates consist of regular crystals. The crystals began to melt at 110 °C and disappeared at 165 °C (Fig. 3(d 1–4)) using hot stage heating. Furthermore, the differential scanning calorimetry (DSC) analysis verifies that the intermediate has a broad melting peak at 164.7 °C (Fig. S2). This is not an indication of pure tetraphenyltin (melt point = 228.53 °C, Fig. S3) or PCL (melt point = 55.74 °C, Fig. S4). Furthermore, polymerized caprolactone at 240 °C for 10 h without using a catalyst only produced a PCL with an Mn of 15300 (Table S2). Therefore, the assumption is made that the intermediates are a complex of tetraphenyltin and pre-polymers. Consequently, tetraphenyltin is significant in accelerating the reaction.

Combining the above experimental results, DFT calculations^[36] were performed to gain further mechanistic insights into this transformation. The possible reaction mechanism is depicted in Fig. 4, which follows the “coordination–insertion” pathway that was reported in several previous studies for the ring-opening transesterification polymerization (ROTEP) of cyclic ester catalyzed by other single-site metal alkoxide complexes.^[37–42] The best catalyst used in this study is tetraphenyltin. The calculations show that the direct insertion of the phenyl group of tetraphenyltin into the coordinated ester monomer has to cross an extremely high activation barrier (45.4 kcal/mol, supporting information (SI)). Therefore, the tetraphenyltin complex is the precatalyst that requires an initiation process to form a real active catalyst (tin–alkoxide complex). The proposed mechanism for catalyst initiation process is shown in Fig. 4(a). First, the small amount of water in the system initiates the caprolactone ring-opening under heat, which results in carboxylic acid. Thereafter, a proto-

bottle (Fig. 3(a)). Fig. 3(b) shows that the supernate is acidic. The separated intermediates and supernate were further analyzed using proton nuclear magnetic resonance (¹H-NMR). Fig. 3(c) presents the ¹H-NMR patterns of benzene has fallen off the catalyst. The characteristic absorption peaks of hydroxyl and methylene in PCL are observed, which indicates the presence of linear oligomers.

providing the proton. This leads to the tin–carbonate complex and releases a benzene ring from the tin center. This is consistent with the experimental results that showed a small



amount of benzene. Subsequently, another molecule of caprolactone reacts with the tin–carbonate complex to form the tin–alkoxide complex. This is an active catalyst for the following propagation process. Notably, step 3 of Fig. 4(a) shows that an anhydride bond (CO–O–CO) was formed at the end of the tin–alkoxide complex. This aligns with the cationic fragment structure that is shown in Fig. 2. This step follows the “coordination–insertion” pathway, and the corresponding energetic details are given in the SI.

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Figure 4. (a) Proposed mechanism for catalyst initiation process. (b) “Coordination–insertion” mechanism for the propagation.

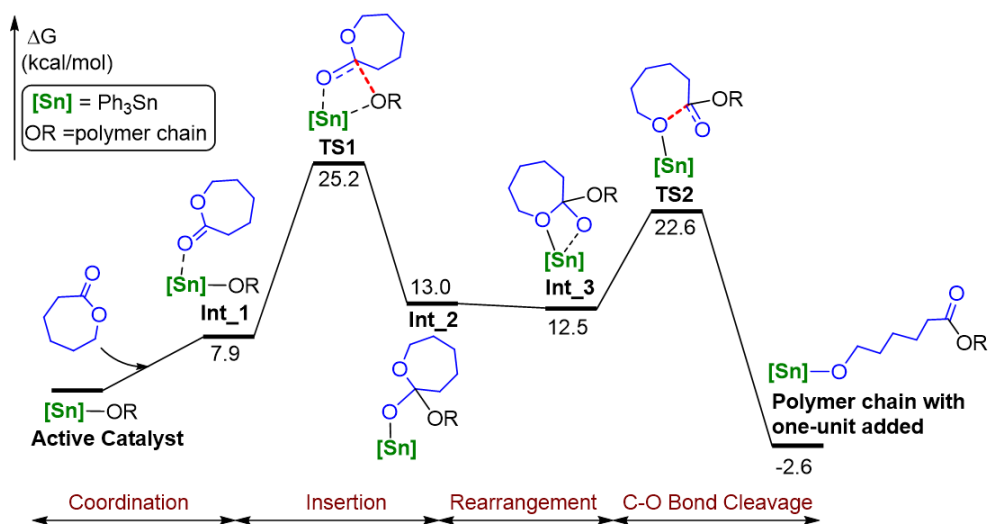


Figure 5. Free energy profile of propagation process along the “coordination–insertion” pathway.

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Fig. 4(b) shows the “coordination–insertion” mechanism for the propagation process. The corresponding free energy profile is given in Fig. 5. Initially, the coordination of caprolactone to the tin center forms a precomplex (**Int_1**), which increases the free energy by 7.9 kcal/mol. The insertion of the alkoxyl group into the activated caprolactone monomer follows via **TS1**, which crosses a free energy activation barrier of 25.2 kcal/mol. Subsequently, the tetrahedral intermediate is rearranged by rotating around the C–O bond (**Int_2** to **Int_3**).

This results in the oxygen atom in the ring approaching the tin center, which decreases the free energy by 0.5 kcal/mol. The C–O bond cleavage then undergoes through **TS2** with a free energy activation barrier of 22.6 kcal/mol. Thereby completing the ring-opening process and generates the polymer chain alkoxide terminus that is elongated by one unit. The overall propagation step is thermodynamically favorable with a free energy decrease of 2.6 kcal/mol, in which the turnover-limiting (TOL) step is the insertion step.

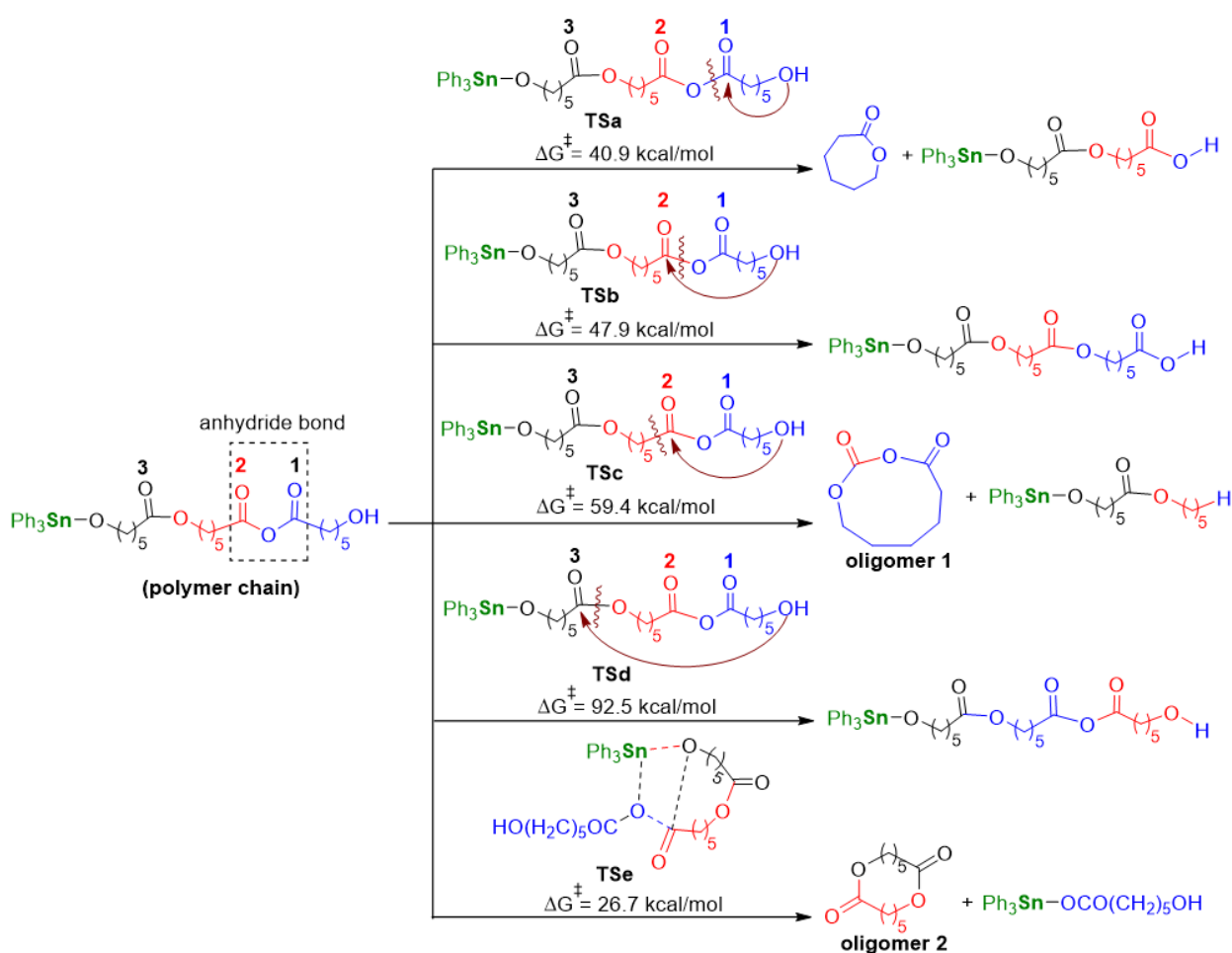


Figure 6. Possible “back-biting” reactions of the tetraphenyltin catalytic system.

The tetraphenyltin catalyst shows good experimental performance for suppressing the formation of oligomers. Generally, the oligomers are caused by the “back-biting” side reactions. Therefore, all possible “back-biting” modes for the tetraphenyltin catalyst were examined. Fig. 6 shows that the activation barriers of all “back-biting” modes of the hydroxyl

terminal at either the anhydride bond (**TSa**, **TSb**, **TSc**) or the further ester bond (**TSd**) are very high (>40 kcal/mol). Among these “back-biting” modes (**TSa–TSd**), only **TSc** could produce a cyclic oligomer side product (oligomer 1). However, **TSc** can be excluded because of the extremely high activation barrier (59.4 kcal/mol). Therefore, the “back-biting” of the terminal hydroxyl group is unlikely to occur and generate oligomers.

Another typical “back-biting” reaction that causes cyclic oligomers for most previous catalytic systems is the “back-biting” of the terminal ester bond at the metal-oxygen bond (see SI). The current Sn(IV) system has an anhydride bond at the terminal end of the polymer chain. The “back-biting” of the anhydride bond at the Sn–oxygen bond occurs through **TSe**, which leads to a cyclic oligomer side product (oligomer 2). Although the activation barrier of **TSe** (26.7 kcal/mol) is 1.5 kcal/mol less favorable than that of the insertion (rate-limiting) step for propagation (**TS1**, 25.2 kcal/mol), the formation of the low content of cyclic oligomers could not be fully excluded. This corresponds to the experimental observation (oligomers content of 7.466 wt.%). The “back-biting” at the Sn–O bond of the internal ester bond of the polymer chain is even more unfavorable with a higher activation barrier of 29.9 kcal/mol (Fig. S9 in SI). The relative free energies of these two transition states (“back-biting” and

insertion) were also compared for a previous typical Sn(II) catalyst.^[43] These free energies deliver comparable results. The insertion is only slightly more favorable (0.5 kcal/mol) than the “back-biting” (Fig. S10 in SI), indicating that the “back-biting” side reaction is competitive with the propagation process in the Sn(II) system. This rationalizes that the Sn(II) catalyst is not effective as the current Sn(IV) catalyst to suppress the formation of cyclic oligomers. Overall, in the current Sn(IV) catalytic system, the end hydroxyl group is unlikely to experience “back-biting” at the adjacent anhydride bond or the further ester bond, which generates oligomers. Furthermore, another type of “back-biting” at the Sn–O bond by either the terminal anhydride bond or the internal ester bond is also less favorable than the insertion step for the propagation process. The above-calculated results sufficiently verify that the current Sn(IV) catalyst efficiently restricts oligomer formation.

4. Conclusions

In summary, this study effectively solved an ongoing trade-off between the high molecular weight, narrow PDI, and low content of oligomers when preparing PCLs. Tetraphenyltin is the best catalyst for preparing high-performance PCL that possesses the highest Mn (65000), narrowest PDI (1.37), and the lowest content of oligomers (7.466 wt.%). Furthermore, the elongation and tensile strength reached 2000% and 38.5 MPa, respectively. **This is significantly better than the reported and other lab-prepared products.** Additionally, by combining the characterization of key intermediates and DFT studies, the detailed reaction mechanism was determined to follow the coordination–insertion pathway. DFT studies further revealed that all possible “back-biting” modes that can generate cyclic oligomers were less favorable than the propagation process. This sufficiently supports the effectiveness of the tetraphenyltin catalyst to suppress the formation of oligomers. Furthermore, this catalyst showed similar performance in synthesizing PA6 using caprolactam as starting monomers, which is still ongoing in our lab. Therefore, this work could provide a scalable synthetic approach towards high-performance polymers.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

This research was supported by the National Key Research Program of China (grant number 2016YFB0302702); National Natural Science Foundation of China (21903022); Scientific Research Foundation of Hunan Provincial Education Department (grant numbers 17A126); and the Open

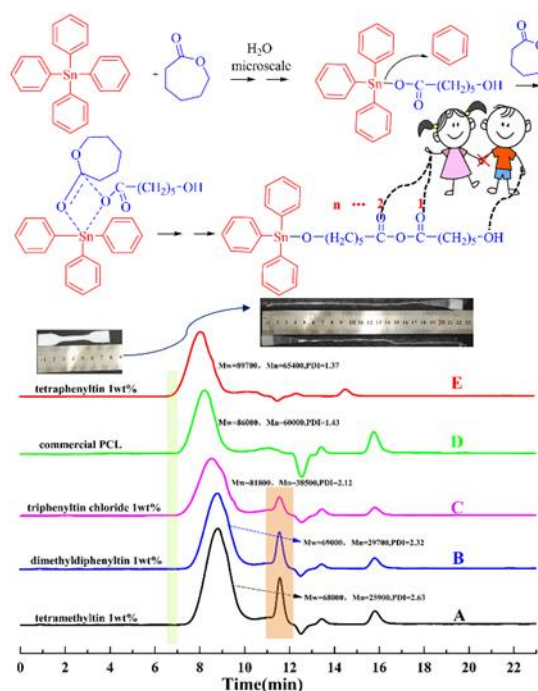
Foundation of National & Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources (grant numbers KF201804). We also sincerely thank Mr. Yi Yang, manager of Su Zhou Newman Analytical Instrument Company to provide low field nuclear magnetic test.

References

- Chang, S. H.; Lee, H. J.; Park, S.; Kim, Y.; Jeong, B., Fast Degradable Polycaprolactone for Drug Delivery. *Biomacromolecules* 2018, 19 (6), 2302-2307.
- Doan-Nguyen, T. P.; Natsathaporn, P.; Jenjob, R.; Niyom, Y.; Ittisanronnachai, S.; Flood, A.; Crespy, D., Regulating Payload Release from Hybrid Nanocapsules with Dual Silica/Polycaprolactone Shells. *Langmuir* 2019, 35 (35), 11389-11396.
- Rashad, A.; Mohamed-Ahmed, S.; Ojansivu, M.; Berstad, K.; Yassin, M. A.; Kivijarvi, T.; Heggset, E. B.; Syverud, K.; Mustafa, K., Coating 3D Printed Polycaprolactone Scaffolds with Nanocellulose Promotes Growth and Differentiation of Mesenchymal Stem Cells. *Biomacromolecules* 2018, 19 (11), 4307-4319.
- Ding, F.; Mou, Q.; Ma, Y.; Pan, G.; Guo, Y.; Tong, G.; Choi, C. H. J.; Zhu, X.; Zhang, C., A Crosslinked Nucleic Acid Nanogel for Effective siRNA Delivery and Antitumor Therapy. *Angew. Chem. Int. Ed.* 2018, 57 (12), 3064-3068.
- Kulkarni, B.; Jayakannan, M., Fluorescent-Tagged Biodegradable Polycaprolactone Block Copolymer FRET Probe for Intracellular Bioimaging in Cancer Cells. *ACS Biomater. Sci. Eng.* 2017, 3 (9), 2185-2197.
- Faleo, C. E. N. R. C. G.; Kevin D. Lance, D. A. B., Qizhi Tang, Desai, T. A., Polycaprolactone Thin-Film Micro- and Nanoporous Cell-Encapsulation Devices. *ACS Nano* 2015, 9 (6), 5675-5682.
- Ding, F.; Mou, Q.; Ma, Y.; Pan, G.; Guo, Y.; Tong, G.; Choi, C. H. J.; Zhu, X.; Zhang, C., A Crosslinked Nucleic Acid Nanogel for Effective siRNA Delivery and Antitumor Therapy. *Angew. Chem. Int. Ed.* 2018, 57 (12), 3064-3068.
- Bhatt, S.; Pulpytel, J.; Mirshahi, M.; Arefi-Khonsari, F., Catalyst-Free Plasma-Assisted Copolymerization of Poly(ϵ -caprolactone)-poly(ethylene glycol) for Biomedical Applications. *ACS Macro Lett.* 2012, 1 (6), 764-767.
- Liu, X.; Miller, A. L.; Fundora, K. A.; Yaszemski, M. J.; Lu, L., Poly(ϵ -caprolactone) Dendrimer Cross-Linked via Metal-Free

- Click Chemistry: Injectable Hydrophobic Platform for Tissue Engineering. *ACS Macro Lett.* 2016, 5 (11), 1261-1265.
- 10 Wang, D.; Jang, J.; Kim, K.; Kim, J.; Park, C. B., "Tree to Bone": Lignin/Polycaprolactone Nanofibers for Hydroxyapatite Biomineralization. *Biomacromolecules* 2019, 20 (7), 2684-2693.
 - 11 No, Y. J.; Castilho, M.; Ramaswamy, Y.; Zreiqat, H., Role of Biomaterials and Controlled Architecture on Tendon/Ligament Repair and Regeneration. *Adv. Mater.* 2020, 32 (18), 1904511-1904527.
 - 12 Su, M.; Li, S.; Zhang, H.; Zhang, J.; Chen, H.; Li, C., Nano-Assemblies from J-Aggregated Dyes: A Stimuli-Responsive Tool Applicable to Living Systems. *J. Am. Chem. Soc.* 2019, 141 (1), 402-413.
 - 13 Sharifi, F.; Patel, B. B.; Dzuilko, A. K.; Montazami, R.; Sakaguchi, D. S.; Hashemi, N., Polycaprolactone Microfibrous Scaffolds to Navigate Neural Stem Cells. *Biomacromolecules* 2016, 17 (10), 3287-3297.
 - 14 Santillán, J.; Dwomoh, E. A.; Rodríguez-Avilés, Y. G.; Bello, S. A.; Nicolau, E., Fabrication and Evaluation of Polycaprolactone Beads-on-String Membranes for Applications in Bone Tissue Regeneration. *ACS Appl. Bio Mater.* 2019, 2 (3), 1031-1040.
 - 15 Kim, S. E.; Wang, J.; Jordan, A. M.; Korley, L. T.; Baer, E.; Pokorski, J. K., Surface Modification of Melt Extruded Poly(epsilon-caprolactone) Nanofibers: Toward a New Scalable Biomaterial Scaffold. *ACS Macro Lett.* 2014, 3 (6), 585-589.
 - 16 Pati, F.; Gantelius, J.; Svahn, H. A., 3D Bioprinting of Tissue/Organ Models. *Angew. Chem. Int. Ed.* 2016, 55 (15), 4650-65.
 - 17 Sanabria-DeLong, N.; Aamer, K. A.; Agrawal, S. K.; Bhatia, S. R.; Tew, G. N., Poly(lactide)-Poly(ethylene oxide)-Poly(lactide) Triblock Copolymers: Synthesis and Thermal Properties. In *Degradable Polymers and Materials*; American Chemical Society: Washington, DC, 2006; pp 156-167.
 - 18 Minna Hakkarainen, A.-C. A., Heterogeneous Biodegradation of Polycaprolactone – Low Molecular Weight Products and Surface Changes. *Macromol. Chem. Phys.* 2002, 203, 1357–1363.
 - 19 Zhu, Y.; Poma, A.; Rizzello, L.; Gouveia, V. M.; Ruiz-Perez, L.; Battaglia, G.; Williams, C. K., Metabolically Active, Fully Hydrolysable Polymersomes. *Angew. Chem. Int. Ed.* 2019, 58 (14), 4581-4586.
 - 20 Zheng, Q.; Li, J.; Yuan, W.; Liu, X.; Tan, L.; Zheng, Y.; Yeung, K. W. K.; Wu, S., Metal–Organic Frameworks Incorporated Polycaprolactone Film for Enhanced Corrosion Resistance and Biocompatibility of Mg Alloy. *ACS Sustainable Chem. Eng.* 2019, 7 (21), 18114-18124.
 - 21 Mahesh Kumar Joshi, A. P. T., Hem Raj Pant, Bishnu K Shrestha, Han Joo Kim, Chan-Hee Park, Cheol Sang Kim, In Situ Generation of Cellulose Nanocrystals in Polycaprolactone Nanofibers: Effects on Crystallinity, Mechanical Strength, Biocompatibility, and Biomimetic Mineralization. *ACS Appl. Mater. Interfaces* 2015, 7 (35), 19672-19683.
 - 22 Williams, D. F., Biocompatibility Pathways: Biomaterials-Induced Sterile Inflammation, Mechanotransduction, and Principles of Biocompatibility Control. *ACS Biomater. Sci. Eng.* 2016, 3 (1), 2-35.
 - 23 Labet, M.; Thielemans, W., Synthesis of polycaprolactone: a review. *Chem. Soc. Rev.* 2009, 38 (12), 3484-3504.
 - 24 Shaheen Motala-Timol, A. B.-L., Dhanjay Jhurry, Kinetic Study of the Al-Schiff's Base Initiated Polymerization of epsilon-caprolactone and Synthesis of Graft Poly(methylmethacrylate-g-caprolactone). *Macromol. Symp.* 2006, 231, 69–80
 - 25 Sherman, R. F. S. J. W., Kinetics and Mechanism of the Stannous Octoate-Catalyzed Bulk Polymerization of epsilon-Caprolactone. *Macromolecules* 2002 35, 1504-1512.
 - 26 Hedrick, M. M. R. K. J. L., Sn(OTf)₂ and Sc(OTf)₃: Efficient and Versatile Catalysts for the Controlled Polymerization of Lactones. *J. Polym. Sci. Part A: Polym. Chem.* 2000, 38 (11), 2067-2074.
 - 27 Lei Zhang, F. N., Russell C. Pratt, Robert M. Waymouth, James L. Hedrick, and Charles G. Wade, Phosphazene Bases: A New Category of Organocatalysts for the Living Ring-Opening Polymerization of Cyclic Esters. *Macromolecules* 2007, 40, 4154-4158.
 - 28 Florjańczyk, Z.; Plichta, A.; Sobczak, M., Ring opening polymerization initiated by methylaluminumoxane/AlMe₃ complexes. *Polymer* 2006, 47 (4), 1081-1090.
 - 29 Peng, S.; Peng, L.; Yi, C.; Zhang, W.; Wang, X., A novel synthetic strategy for preparing semi-aromatic components modified polyamide 6 polymer. *J. Polym. Sci. Part A: Polym. Chem.* 2018, 56 (9), 959-967.
 - 30 Yilgor, I.; Yilgor, E. O. Waterproof, moisture vapor permeable polyurethane urea polymer comprising polycaprolactone and polydimethyl siloxane soft segments. U.S. Patent 5,461,122, October 24, 1995.
 - 31 Albert Ballistreri, D. G., Mario Giuffrida, Giorgio Montaudo', Identification of the ions produced by fast atom bombardment mass spectrometry in some polyesters and polyamides. *Anal. Chem.* 1987, 59 (17), 2024-2027.
 - 32 Vitalini, L. M. G. M. E. S. S. R. D., Organotin-Mediated Synthesis of Macrocyclic Tetraesters. A Combined IH NMR Spectroscopy, Gel Permeation Chromatography, and Fast Atom Bombardment Mass Spectrometry Approach to Complete Product Analysis. *Macromolecules* 1989 22 (8), 3275-3280.
 - 33 Peponi, L.; Navarro-Baena, I.; Sonseca, A.; Gimenez, E.; Marcos-Fernandez, A.; Kenny, J. M., Synthesis and characterization of PCL–PLLA polyurethane with shape memory behavior. *Eur. Polym. J.* 2013, 49 (4), 893-903.
 - 34 Besghini, D.; Mauri, M.; Simonutti, R., Time Domain NMR in Polymer Science: From the Laboratory to the Industry. *Appl. Sci.* 2019, 9 (9), 1801-1834.
 - 35 Tian, M. K. S. Y. Y., Energy Gaps and their Control in Thiophene - Based Polymers and Oligomers. In *Handbook of Thiophene-based Materials: Applications in Organic Electronics and Photonics*; John Wiley & Sons, Ltd: New York, 2009; pp 341-364.
 - 36 DFT calculations were performed under the level of (SMD)-M06/6-311++G(d,p)-SDD//B3LYP-D3(BJ)/6-31G(d,p)-SDD by Gaussian program. See SI for computational details.
 - 37 Edward L. Marshall, V. C. G., Henry S. Rzepa, A Computational Analysis of the Ring-Opening Polymerization of rac -Lactide Initiated by Single-Site α -Diketiminato Metal Complexes: Defining the Mechanistic Pathway and the Origin of Stereocontrol. *J. Am. Chem. Soc.* 2005, 127 (16), 6048-6051.
 - 38 Jitonnorn, J.; Molloy, R.; Punyodom, W.; Meelua, W., Theoretical studies on aluminum trialkoxide-initiated lactone ring-opening polymerizations: Roles of alkoxide substituent and monomer ring structure. *Comput. Theor. Chem.* 2016, 1097, 25-32.
 - 39 Marlier, E. E.; Macaranas, J. A.; Marell, D. J.; Dunbar, C. R.; Johnson, M. A.; DePorre, Y.; Miranda, M. O.; Neisen, B. D.; Cramer, C. J.; Hillmyer, M. A.; Tolman, W. B., Mechanistic Studies of epsilon-Caprolactone Polymerization by (salen)AlOR Complexes and a Predictive Model for Cyclic Ester Polymerizations. *ACS Catal.* 2016, 6 (2), 1215-1224.
 - 40 Wei, J.; Riffel, M. N.; Diaconescu, P. L., Redox Control of Aluminum Ring-Opening Polymerization: A Combined

- Experimental and DFT Investigation. *Macromolecules* 2017, 50 (5), 1847-1861.
- 41 Macaranas, J. A.; Luke, A. M.; Mandal, M.; Neisen, B. D.; Marell, D. J.; Cramer, C. J.; Tolman, W. B., Sterically Induced Ligand Framework Distortion Effects on Catalytic Cyclic Ester Polymerizations. *Inorg. Chem.* 2018, 57 (6), 3451-3457.
- 42 Mandal, M.; Luke, A. M.; Dereli, B.; Elwell, C. E.; Reineke, T. M.; Tolman, W. B.; Cramer, C. J., Computational Prediction and Experimental Verification of ϵ -Caprolactone Ring-Opening Polymerization Activity by an Aluminum Complex of an Indolide/Schiff-Base Ligand. *ACS Catal.* 2018, 9 (2), 885-889.
- 43 Sattayanon, C.; Kungwan, N.; Punyodom, W.; Meepowpan, P.; Jungsuttiwong, S., Theoretical investigation on the mechanism and kinetics of the ring-opening polymerization of epsilon-caprolactone initiated by tin(II) alkoxides. *J. Mol. Graphics Modell.* 2013, 19 (12), 5377-5385



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ARTICLE

Effective Regulation of Polycaprolactone Molecular Weight and Oligomers Content Using Tetraphenyltin Catalyst

Caihong Gong^{ac}, Jinxia Li^b, Chunwang Yi^{*ac}, Shuanglin Qu^{*b}

There is a lack of effective approaches that produce polycaprolactone materials (PCL) with a high molecular weight, narrow polymer dispersity index (PDI), and fewer formation of oligomers. The immigration of the remained oligomers predominantly causes poor PCL quality and induces odor release. This limits the extensive application of PCL materials. This study investigates the effects of different catalysts and loadings on the PCL performance along with the formation of oligomers in detail. The oligomers were successfully separated using gel permeation chromatography (GPC). This was followed by a quantitative and qualitative identification using high-resolution mass spectrometry (HRMS) and low field nuclear magnetic (L-field NMR) analysis. The results show that tetraphenyltin is an effective catalyst to promote the reaction and produce high-performance PCL that possesses the highest M_n (65000), narrowest PDI (1.37), and the lowest content of oligomers (7.466 wt.%). Density functional theory (DFT) studies that were combined with characterizing key intermediates verified that an anhydride bond was formed close to the end hydroxyl group in the PCL chain because of the special catalytic mechanism. This unusual chemical structure successfully inhibited the chain from being broken by the “back-biting” behavior, which is helpful for lowering the content of oligomers. This study can provide a scalable synthetic approach to creating high-performance polymers.

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1. Introduction

The main paragraph text follows directly on here. Polycaprolactone (PCL) has various biological applications, such as being a controlled drug release carrier,^[1-4] fluorescent probe,^[5] cell-encapsulation device,^[6] tissue culture bed frame,^[7-11] biological dye,^[12] and medical modeling material.^[8, 13-16] This is because of its excellent biodegradation^[17-19] and biocompatibility.^[20-22] Several studies have reported that minimal water, oxygen, and hydroxy compounds can initiate the ring-opening polymerization of caprolactone.^[23] However, this can only produce low molecular weight PCL in the absence of a catalyst. Similarly, most catalysts such as diisopropyl amino lithium,^[24] stannous octoate,^[25] and organic acid tin [Sn(OTf)₂]^[26] insignificantly influence synthesis during caprolactone polymerization. These catalysts can only be used to prepare PCL with a molecular weight (Mn) varying from 4000 to 15200. Furthermore, most of the prepared PCLs have a wide polymer dispersity index (PDI) owing to the generation of oligomers, or the simultaneous polymerization and degradation during polymerization. Although phosphazene bases can generate PCL with a high Mn (≈ 38000), the conversion rate was only 14% when reacting with caprolactone for more than 10 days at 80 °C.^[27] Methylaluminoxane-trimethylaluminum is a rare catalyst that can increase the Mn of PCL to 223800.^[28] However, the "back-biting" side reaction is competitive with the caprolactone polymerization process. This generates cyclic oligomers and makes the PCL similar to polyamide 6 (PA6),^[29] which contains certain quantities of oligomers. The authors did not investigate the mechanic performance of the prepared PCL and the negative effects of cyclic oligomers on the PCL properties further.

The solubility in organic solvents and the melting point of oligomers were close to PCL. This made the substances difficult to separate. Generally, the remaining oligomers can damage the material performance and release unpleasant odors after migrating progressively to the surface of the materials. This limits the application and development of PCL significantly.^[30] Recent developments in technology include gel permeation chromatography (GPC) and mass spectrum (MS) technologies. These approaches have been used to identify and determine the oligomers.^[31-32] However, an effective method to suppress the formation of oligomers have not been proposed. Therefore, significant challenges exist in PCL performance improvement, especially for the regulation of the content of oligomers, molecular weight, and PDI of the PCL. Therefore, a new technology using a tetraphenyltin (Ph₄Sn) catalyst to prepare high-performing PCL is reported in this study. The molecular weight and the mechanical properties of PCL and the oligomer content could be conveniently regulated through varying tetraphenyltin loadings. Furthermore, characterization of key reaction intermediates and density functional theory (DFT) studies revealed the detailed reaction mechanism and verified that the catalyst can effectively suppress the formation of oligomers.

2. Experiment

2.1 Polymerization

The polymerization tests were performed using a "one-pot" method. Caprolactone and catalyst were added to a four-neck round bottle in a fixed mass ratio. Polymerization followed at 200 °C for 10 h in nitrogen air according to the synthetic approach shown in Fig. 1(a). Catalysts with different steric hindrance, such as tetraphenyltin, triphenyltin chloride, dimethyldiphenyltin, and tetramethyltin, were selected to synthesize the PCL. The main influencing factors of the polymerization process were investigated. These include the effects of different reaction times (2–14 h), temperature (100–240 °C), and catalyst dosage (0.1–5% by weight) on the polymerization process. Other reactions were avoided using nitrogen protection that was used in the experiment. After synthesized, the products were pulverized into fine particles and dried to a constant weight at 40 °C in vacuum conditions for further analysis. All reaction process parameters are listed in Table S1.

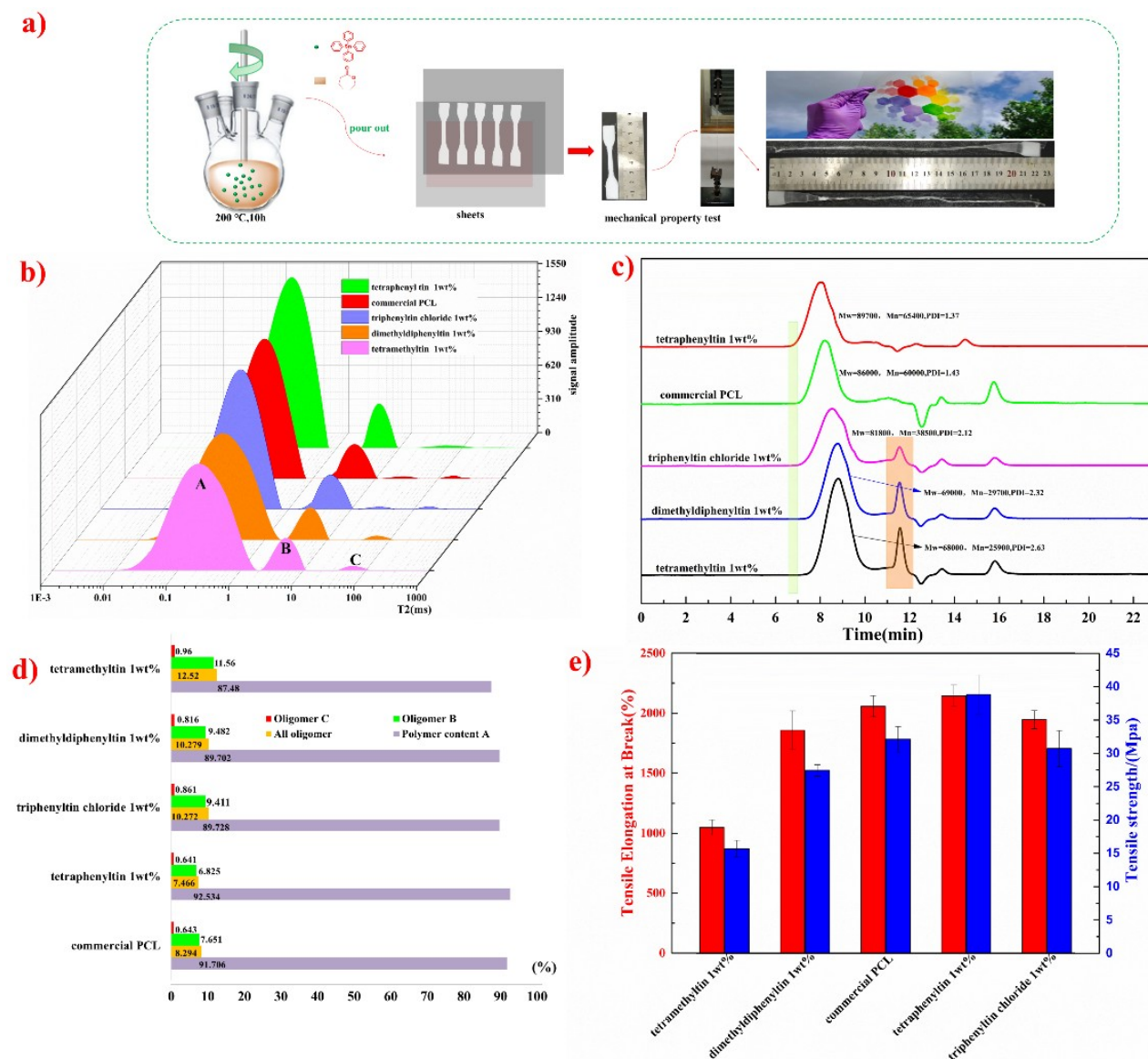


Figure 1. a) Synthesis route, Dumb-bell samples before and after tensile strength test (tetraphenyltin catalyst). b) Low field NMR patterns: "A" means long chain segment, "B" and "C" means small molecular chain segment. c) GPC curves. d) High-resolution mass spectrogram of oligomers. e) Mechanical properties.

3. Results and discussion

The conclusions section should come in this section at the end of the article, before the acknowledgements. The PCL properties were obtained using a 1 wt.% catalyst mass ratio under the same reaction conditions (200 °C, 10 h). These are displayed in Fig. 1 and Table S2. The GPC results (Fig. 1(c)) show that the tetraphenyltin system produces PCL with the highest Mn (65000) and the narrowest PDI

(1.37). Additionally, small peaks appeared during the retention time of 11–16 min. This demonstrated that a certain number of oligomers with a molecular weight of less than 2000 was produced during the PCL synthesis.^[33] The content of polymers and oligomers in the PCL was measured further using low field nuclear magnetic (L-field NMR) analysis.^[34] This indicated that the tetraphenyltin catalyzed PCL has the lowest oligomers content (7.466 wt. %, Fig. 1(b)), which is comparable to that of the current

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commercial PCL. However, the PCL resulted from tetraphenyltin catalyst is vastly superior to other lab-prepared PCLs that were produced by using the other three catalysts and most reported catalysts.^[23, 25] Furthermore, the results indicate that the oligomers content greatly influences the properties of the PCL. Higher content of oligomers leads to worse mechanical properties. Notably, the strain–stress tests show that the elongation and tensile strength of the tetraphenyltin catalyzed PCL reached 2000% and 38.5 MPa, respectively (Fig. 1(a, e)). This is also significantly better than current commercial (and the other lab-prepared) products. Especially, compared to the reported products with best elongation of 900%, the elongation is remarkably increased []. Besides, the tetraphenyltin catalyzed PCL was stable without peculiar smell after exposed to natural condition for half a year. However, the other lab-prepared PCLs released odor after only being kept for days, owing to the immigration of the remained oligomers. Therefore, tetraphenyltin is the best catalyst for producing PCL polymer that has optimum properties. The optimum process conditions for the PCL preparation were investigated further. A 1 wt.% dosage of tetraphenyltin was maintained for 10 h at 200 °C (Fig. 1, Table S2, and Table S3).

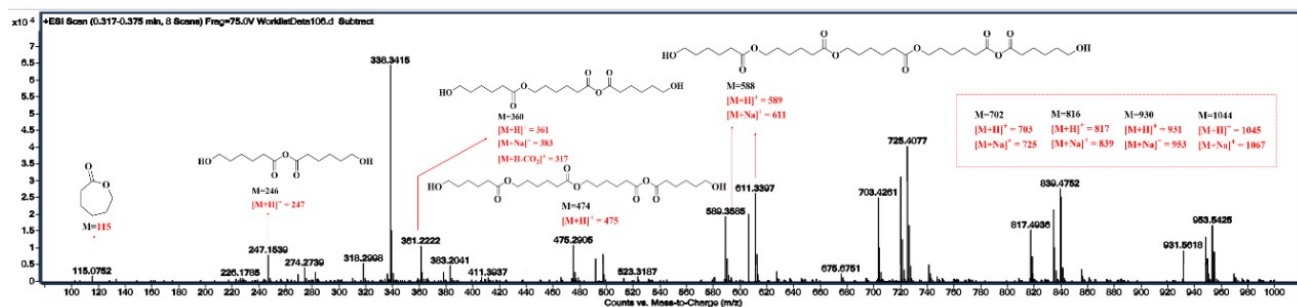
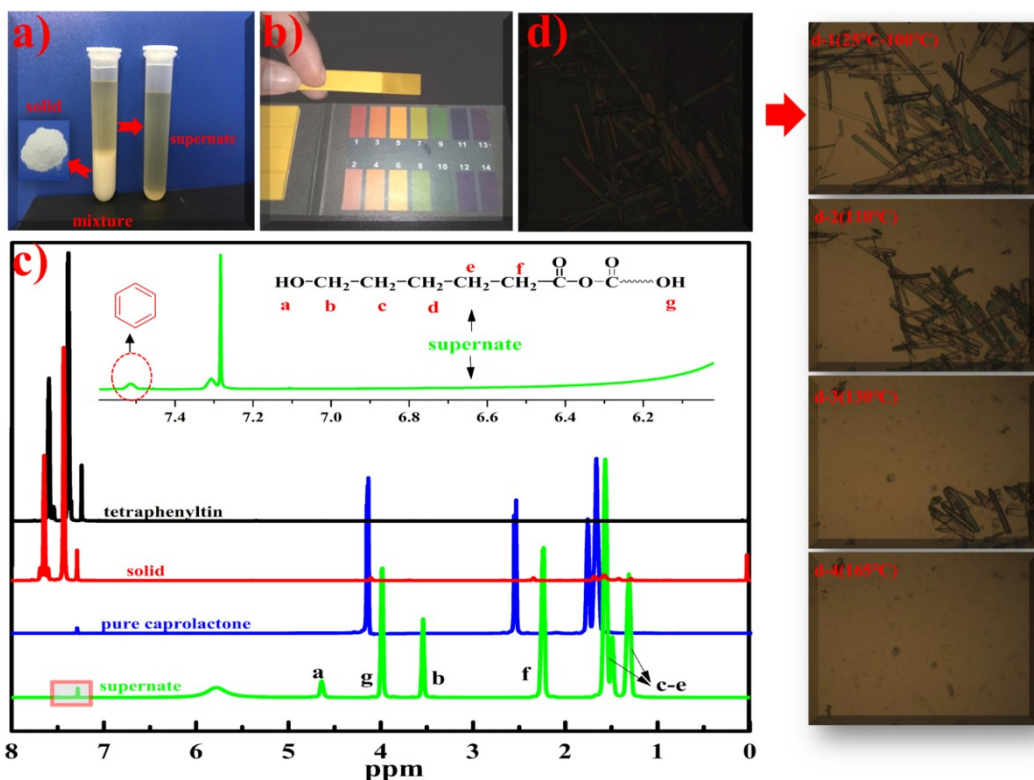


Figure 2. High-resolution mass spectrogram of oligomers.

The components related to small peaks that are shown in the GPC analysis (Fig. 1(c)) were collected for further analysis. Fig. 2 is the pattern of the high-resolution mass spectrometer (HRMS) that shows that there is a certain amount of caprolactone in the components. Previous studies have shown that the active end groups (i.e., hydroxyl and amino groups) can attack the ester or amide bonds in the molecular chains through “back-biting”. This results in cyclic oligomers that are shown in Fig. S1.^[23, 29] However, the cyclic dimer, cyclic trimer, and other typical cyclic oligomers of Fig. S1 are absent in the mass spectra. Additionally, ionic fragment peaks that are dissociated from the linear oligomers with the regularity of 114 appear in the spectra. Possible chemical structures are displayed in Fig. 2. A new anhydride bond (CO–O–CO) verifies that a special catalytic mechanism was involved in the reaction. This has been proved through DFT calculations and will be discussed in detail in the following sections. The HRMS result shows that the “back-biting” behavior of the end hydroxyl groups has been effectively restricted, thereby significantly reducing the generation of cyclic oligomers.^[35]

A well-designed experiment was performed to study the possible mechanism for the formation of PCL. White

intermediates were generated after the caprolactone, and tetraphenyltin reacted at 120 °C for 10 h in a four-neck



round bottle (Fig. 3(a)). Fig. 3(b) shows that the supernate is acidic. The separated intermediates and supernate were further analyzed using proton nuclear magnetic resonance (¹H-NMR). Fig. 3(c) presents the ¹H-NMR patterns of benzene has fallen off the catalyst. The characteristic absorption peaks of hydroxyl and methylene in PCL are observed, which indicates the presence of linear oligomers.

Figure 3. a) Intermediate product. b) pH test of supernate. c) Proton nuclear magnetic resonance (^1H NMR) spectra of the bottom solid, supernate, pure caprolactone, and tetraphenyltin. d) Polarizing heat table microscope (POM) image of the separated bottom solid. (d 1–4) Melting behaviors of intermediates under POM at different temperatures.

The intermediates refract colorful light under polarized optical microscopy (Fig. 3(d)), which indicates that the intermediates consist of regular crystals. The crystals began to melt at 110 °C and disappeared at 165 °C (Fig. 3(d 1–4)) using hot stage heating. Furthermore, the differential scanning calorimetry (DSC) analysis verifies that the intermediate has a broad melting peak at 164.7 °C (Fig. S2). This is not an indication of pure tetraphenyltin (melt point = 228.53 °C, Fig. S3) or PCL (melt point = 55.74 °C, Fig. S4). Furthermore, polymerized caprolactone at 240 °C for 10 h without using a catalyst only produced a PCL with an Mn of 15300 (Table S2). Therefore, the assumption is made that the intermediates are a complex of tetraphenyltin and pre-polymers. Consequently, tetraphenyltin is significant in accelerating the reaction.

Combining the above experimental results, DFT calculations^[36] were performed to gain further mechanistic insights into this transformation. The possible reaction mechanism is depicted in Fig. 4, which follows the “coordination–insertion” pathway that was reported in several previous studies for the ring–opening transesterification polymerization (ROTEP) of cyclic ester catalyzed by other single-site metal alkoxide complexes.^[37–42] The best catalyst used in this study is tetraphenyltin. The calculations show that the direct insertion of the phenyl group of tetraphenyltin into the coordinated ester monomer has to cross an extremely high activation barrier (45.4 kcal/mol, supporting information (SI)). Therefore, the tetraphenyltin complex is the precatalyst that requires an initiation process to form a real active catalyst (tin–alkoxide complex). The proposed mechanism for catalyst initiation process is shown in Fig. 4(a). First, the small amount of water in the system initiates the caprolactone ring–opening under heat, which results in carboxylic acid. Thereafter, a proto-demetalation step undergoes with the carboxylic acid providing the proton. This leads to the tin–carbonate complex and releases a benzene ring from the tin center. This is consistent with the experimental results that showed a small amount of benzene. Subsequently, another molecule of caprolactone reacts with the tin–carbonate complex to form the tin–alkoxide complex. This is an active catalyst for the following propagation process. Notably, step 3 of Fig. 4(a) shows that an anhydride bond (CO–O–CO) was formed at the end of the tin–alkoxide complex. This aligns with the cationic fragment structure that is shown in Fig. 2. This step follows the “coordination–insertion” pathway, and the corresponding energetic details are given in the SI.

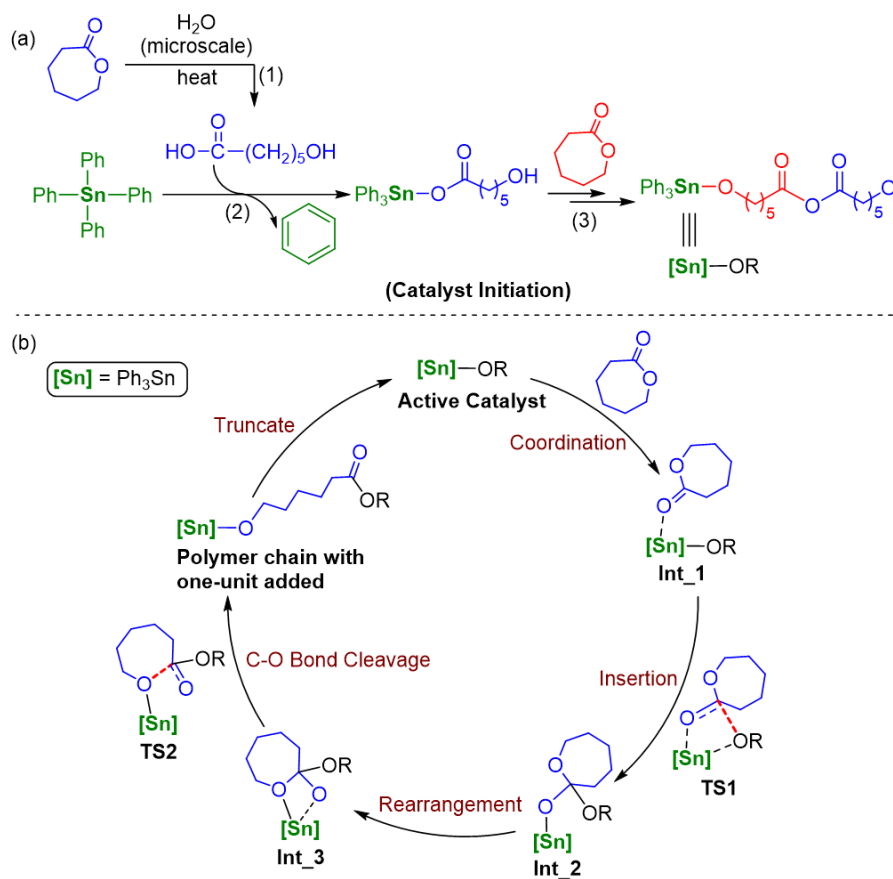


Figure 4. (a) Proposed mechanism for catalyst initiation process. (b) “Coordination–insertion” mechanism for the propagation.

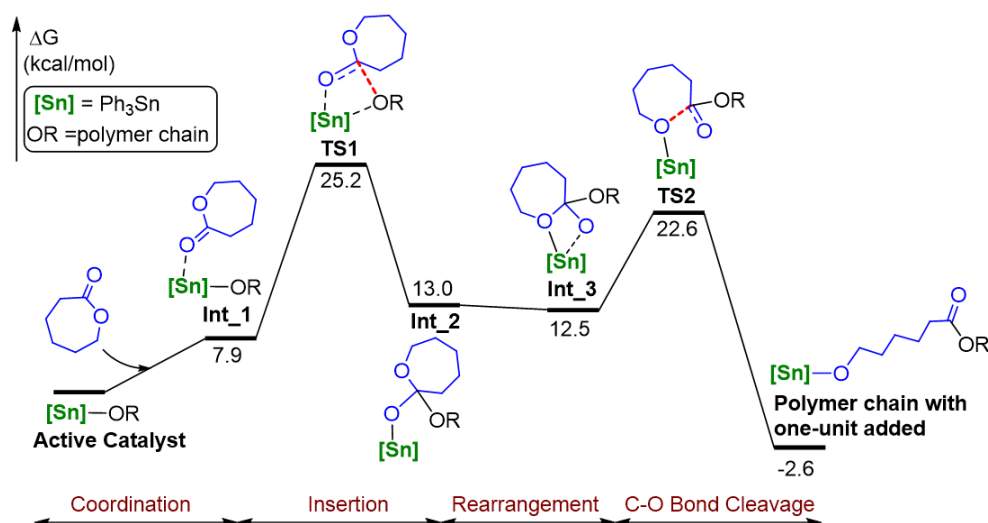


Figure 5. Free energy profile of propagation process along the “coordination–insertion” pathway.

Fig. 4(b) shows the “coordination–insertion” mechanism for the propagation process. The corresponding free energy profile is given in Fig. 5. Initially, the coordination of caprolactone to the tin center forms a precomplex (Int_1), which increases the free energy by 7.9 kcal/mol. The insertion of the alkoxyl group into the activated caprolactone monomer follows via $TS1$, which crosses a free energy activation barrier of 25.2 kcal/mol. Subsequently, the tetrahedral intermediate is rearranged by rotating around the C–O bond (Int_2 to Int_3). This results

in the oxygen atom in the ring approaching the tin center, which decreases the free energy by 0.5 kcal/mol. The C–O bond cleavage then undergoes through $TS2$ with a free energy activation barrier of 22.6 kcal/mol. Thereby completing the ring-opening process and generates the polymer chain alkoxide terminus that is elongated by one unit. The overall propagation step is thermodynamically favorable with a free energy decrease of 2.6 kcal/mol, in which the turnover-limiting (TOL) step is the insertion step.

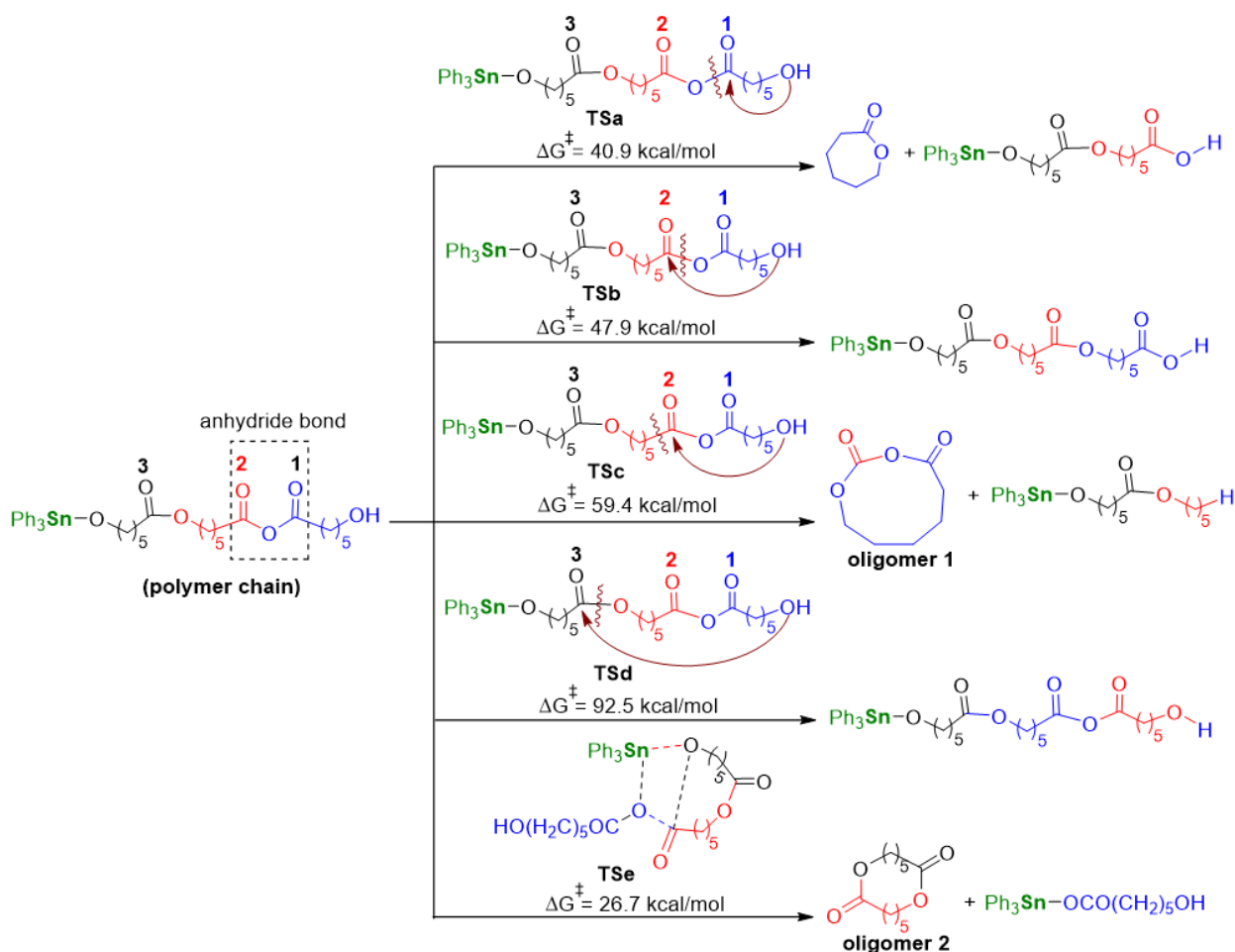


Figure 6. Possible "back-biting" reactions of the tetraphenyltin catalytic system.

The tetraphenyltin catalyst shows good experimental performance for suppressing the formation of oligomers. Generally, the oligomers are caused by the "back-biting" side reactions. Therefore, all possible "back-biting" modes for the tetraphenyltin catalyst were examined. Fig. 6 shows that the activation barriers of all "back-biting" modes of the hydroxyl terminal at either the anhydride bond (**TSa**, **TSb**, **TSc**) or the further ester bond (**TSd**) are very high (>40 kcal/mol). Among these "back-biting" modes (**TSa-TSd**), only **TSc** could produce a cyclic oligomer side product (oligomer 1). However, **TSc** can be excluded because of the extremely high activation barrier (59.4 kcal/mol). Therefore, the "back-biting" of the terminal hydroxyl group is unlikely to occur and generate oligomers. Another typical "back-biting" reaction that causes cyclic oligomers for most previous catalytic systems is the "back-biting" of the terminal ester bond at the metal-oxygen bond (see SI). The current Sn(IV) system has an anhydride bond at the terminal end of the polymer chain. The "back-biting" of the anhydride bond at the Sn-oxygen bond occurs through **TSe**, which leads to a cyclic oligomer side product (oligomer 2).

Although the activation barrier of **TSe** (26.7 kcal/mol) is 1.5 kcal/mol less favorable than that of the insertion (rate-limiting) step for propagation (**TS1**, 25.2 kcal/mol), the formation of the low content of cyclic oligomers could not be fully excluded. This corresponds to the experimental observation (oligomers content of 7.466 wt.%). The "back-biting" at the Sn-O bond of the internal ester bond of the polymer chain is even more unfavorable with a higher activation barrier of 29.9 kcal/mol (Fig. S9 in SI). The relative free energies of these two transition states ("back-biting" and insertion) were also compared for a previous typical Sn(II) catalyst.^[43] These free energies deliver comparable results. The insertion is only slightly more favorable (0.5 kcal/mol) than the "back-biting" (Fig. S10 in SI), indicating that the "back-biting" side reaction is competitive with the propagation process in the Sn(II) system. This rationalizes that the Sn(II) catalyst is not effective as the current Sn(IV) catalyst to suppress the formation of cyclic oligomers. Overall, in the current Sn(IV) catalytic system, the end hydroxyl group is unlikely to experience "back-biting" at the adjacent anhydride bond or the further ester bond, which generates oligomers.

Furthermore, another type of “back-biting” at the Sn–O bond by either the terminal anhydride bond or the internal ester bond is also less favorable than the insertion step for

the propagation process. The above-calculated results sufficiently verify that the current Sn(IV) catalyst efficiently restricts oligomer formation.

4. Conclusions

In summary, this study effectively solved an ongoing trade-off between the high molecular weight, narrow PDI, and low content of oligomers when preparing PCLs. Tetraphenyltin is the best catalyst for preparing high-performance PCL that possesses the highest Mn (65000), narrowest PDI (1.37), and the lowest content of oligomers (7.466 wt.%). Furthermore, the elongation and tensile strength reached 2000% and 38.5 MPa, respectively. **This is significantly better than the reported and other lab-prepared products.** Additionally, by combining the characterization of key intermediates and DFT studies, the detailed reaction mechanism was determined to follow the coordination–insertion pathway. DFT studies further revealed that all possible “back-biting” modes that can generate cyclic oligomers were less favorable than the propagation process. This sufficiently supports the effectiveness of the tetraphenyltin catalyst to suppress the formation of oligomers. Furthermore, this catalyst showed similar performance in synthesizing PA6 using caprolactam as starting monomers, which is still ongoing in our lab. Therefore, this work could provide a scalable synthetic approach towards high-performance polymers.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

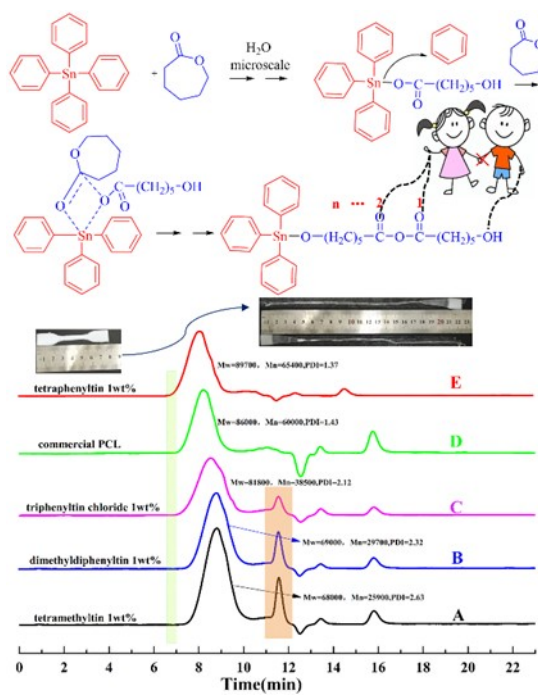
This research was supported by the National Key Research Program of China (grant number 2016YFB0302702); National Natural Science Foundation of China (21903022); Scientific Research Foundation of Hunan Provincial Education Department (grant numbers 17A126); and the Open Foundation of National & Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources (grant numbers KF201804). We also sincerely thank Mr. Yi Yang, manager of Su Zhou Newman Analytical Instrument Company to provide low field nuclear magnetic test.

References

- 1 Chang, S. H.; Lee, H. J.; Park, S.; Kim, Y.; Jeong, B., Fast Degradable Polycaprolactone for Drug Delivery. *Biomacromolecules* 2018, 19 (6), 2302-2307.

- 2 Doan-Nguyen, T. P.; Natsathaporn, P.; Jenjob, R.; Niyom, Y.; Ittisanronnachai, S.; Flood, A.; Crespy, D., Regulating Payload Release from Hybrid Nanocapsules with Dual Silica/Polycaprolactone Shells. *Langmuir* 2019, 35 (35), 11389-11396.
- 3 Rashad, A.; Mohamed-Ahmed, S.; Ojansivu, M.; Berstad, K.; Yassin, M. A.; Kivijarvi, T.; Heggset, E. B.; Syverud, K.; Mustafa, K., Coating 3D Printed Polycaprolactone Scaffolds with Nanocellulose Promotes Growth and Differentiation of Mesenchymal Stem Cells. *Biomacromolecules* 2018, 19 (11), 4307-4319.
- 4 Ding, F.; Mou, Q.; Ma, Y.; Pan, G.; Guo, Y.; Tong, G.; Choi, C. H. J.; Zhu, X.; Zhang, C., A Crosslinked Nucleic Acid Nanogel for Effective siRNA Delivery and Antitumor Therapy. *Angew. Chem. Int. Ed.* 2018, 57 (12), 3064-3068.
- 5 Kulkarni, B.; Jayakannan, M., Fluorescent-Tagged Biodegradable Polycaprolactone Block Copolymer FRET Probe for Intracellular Bioimaging in Cancer Cells. *ACS Biomater. Sci. Eng.* 2017, 3 (9), 2185-2197.
- 6 Faleo, C. E. N. R. C. G.; Kevin D. Lance, D. A. B., Qizhi Tang, Desai, T. A., Polycaprolactone Thin-Film Micro- and Nanoporous Cell-Encapsulation Devices. *ACS Nano* 2015, 9 (6), 5675-5682.
- 7 Reddy, C. S.; Venugopal, J. R.; Ramakrishna, S.; Zussman, E., Polycaprolactone/oligomer compound scaffolds for cardiac tissue engineering. *J. Biomed. Mater. Res., Part A* 2014, 102 (10), 3713-3725.
- 8 Bhatt, S.; Pulpytel, J.; Mirshahi, M.; Arefi-Khonsari, F., Catalyst-Free Plasma-Assisted Copolymerization of Poly(ϵ -caprolactone)-poly(ethylene glycol) for Biomedical Applications. *ACS Macro Lett.* 2012, 1 (6), 764-767.
- 9 Liu, X.; Miller, A. L.; Fundora, K. A.; Yaszemski, M. J.; Lu, L., Poly(ϵ -caprolactone) Dendrimer Cross-Linked via Metal-Free Click Chemistry: Injectable Hydrophobic Platform for Tissue Engineering. *ACS Macro Lett.* 2016, 5 (11), 1261-1265.
- 10 Wang, D.; Jang, J.; Kim, K.; Kim, J.; Park, C. B., "Tree to Bone": Lignin/Polycaprolactone Nanofibers for Hydroxyapatite Biomineralization. *Biomacromolecules* 2019, 20 (7), 2684-2693.
- 11 No, Y. J.; Castilho, M.; Ramaswamy, Y.; Zreiqat, H., Role of Biomaterials and Controlled Architecture on Tendon/Ligament Repair and Regeneration. *Adv. Mater.* 2020, 32 (18), 1904511-1904527.
- 12 Su, M.; Li, S.; Zhang, H.; Zhang, J.; Chen, H.; Li, C., Nano-Assemblies from J-Aggregated Dyes: A Stimuli-Responsive Tool Applicable To Living Systems. *J. Am. Chem. Soc.* 2019, 141 (1), 402-413.
- 13 Sharifi, F.; Patel, B. B.; Dzuilko, A. K.; Montazami, R.; Sakaguchi, D. S.; Hashemi, N., Polycaprolactone Microfibrous Scaffolds to Navigate Neural Stem Cells. *Biomacromolecules* 2016, 17 (10), 3287-3297.
- 14 Santillán, J.; Dwomoh, E. A.; Rodríguez-Avilés, Y. G.; Bello, S. A.; Nicolau, E., Fabrication and Evaluation of Polycaprolactone Beads-on-String Membranes for Applications in Bone Tissue Regeneration. *ACS Appl. Bio Mater.* 2019, 2 (3), 1031-1040.
- 15 Kim, S. E.; Wang, J.; Jordan, A. M.; Korley, L. T.; Baer, E.; Pokorski, J. K., Surface Modification of Melt Extruded Poly(ϵ -caprolactone) Nanofibers: Toward a New Scalable Biomaterial Scaffold. *ACS Macro Lett.* 2014, 3 (6), 585-589.

- 16 Pati, F.; Gantelius, J.; Svahn, H. A., 3D Bioprinting of Tissue/Organ Models. *Angew. Chem. Int. Ed.* 2016, 55 (15), 4650-65.
- 17 Sanabria-DeLong, N.; Aamer, K. A.; Agrawal, S. K.; Bhatia, S. R.; Tew, G. N., Poly(lactide)-Poly(ethylene oxide)-Poly(lactide) Triblock Copolymers: Synthesis and Thermal Properties. In *Degradable Polymers and Materials*; American Chemical Society: Washington, DC, 2006; pp 156-167.
- 18 Minna Hakkarainen, A.-C. A., Heterogeneous Biodegradation of Polycaprolactone – Low Molecular Weight Products and Surface Changes. *Macromol. Chem. Phys.* 2002, 203, 1357–1363.
- 19 Zhu, Y.; Poma, A.; Rizzello, L.; Gouveia, V. M.; Ruiz-Perez, L.; Battaglia, G.; Williams, C. K., Metabolically Active, Fully Hydrolysable Polymersomes. *Angew. Chem. Int. Ed.* 2019, 58 (14), 4581-4586.
- 20 Zheng, Q.; Li, J.; Yuan, W.; Liu, X.; Tan, L.; Zheng, Y.; Yeung, K. W. K.; Wu, S., Metal–Organic Frameworks Incorporated Polycaprolactone Film for Enhanced Corrosion Resistance and Biocompatibility of Mg Alloy. *ACS Sustainable Chem. Eng.* 2019, 7 (21), 18114-18124.
- 21 Mahesh Kumar Joshi, A. P. T., Hem Raj Pant, Bishnu K Shrestha, Han Joo Kim, Chan-Hee Park, Cheol Sang Kim, In Situ Generation of Cellulose Nanocrystals in Polycaprolactone Nanofibers: Effects on Crystallinity, Mechanical Strength, Biocompatibility, and Biomimetic Mineralization. *ACS Appl. Mater. Interfaces* 2015, 7 (35), 19672-19683.
- 22 Williams, D. F., Biocompatibility Pathways: Biomaterials-Induced Sterile Inflammation, Mechanotransduction, and Principles of Biocompatibility Control. *ACS Biomater. Sci. Eng.* 2016, 3 (1), 2-35.
- 23 Labet, M.; Thielemans, W., Synthesis of polycaprolactone: a review. *Chem. Soc. Rev.* 2009, 38 (12), 3484-3504.
- 24 Shaheen Motala-Timol, A. B.-L., Dhanjay Jhurry, Kinetic Study of the Al-Schiff's Base Initiated Polymerization of ϵ -caprolactone and Synthesis of Graft Poly(methylmethacrylate-g-caprolactone). *Macromol. Symp.* 2006, 231, 69–80.
- 25 Sherman, R. F. S. J. W., Kinetics and Mechanism of the Stannous Octoate-Catalyzed Bulk Polymerization of ϵ -Caprolactone. *Macromolecules* 2002 35, 1504-1512.
- 26 Hedrick, M. M. R. K. J. L., Sn(OTf)₂ and Sc(OTf)₃: Efficient and Versatile Catalysts for the Controlled Polymerization of Lactones. *J. Polym. Sci. Part A: Polym. Chem.* 2000, 38 (11), 2067-2074.
- 27 Lei Zhang, F. N., Russell C. Pratt, Robert M. Waymouth, James L. Hedrick, and Charles G. Wade, Phosphazene Bases: A New Category of Organocatalysts for the Living Ring-Opening Polymerization of Cyclic Esters. *Macromolecules* 2007, 40, 4154-4158.
- 28 Florjańczyk, Z.; Plichta, A.; Sobczak, M., Ring opening polymerization initiated by methylaluminumoxane/AlMe₃ complexes. *Polymer* 2006, 47 (4), 1081-1090.
- 29 Peng, S.; Peng, L.; Yi, C.; Zhang, W.; Wang, X., A novel synthetic strategy for preparing semi-aromatic components modified polyamide 6 polymer. *J. Polym. Sci. Part A: Polym. Chem.* 2018, 56 (9), 959-967.
- 30 Yilgor, I.; Yilgor, E. O. Waterproof, moisture vapor permeable polyurethane urea polymer comprising polycaprolactone and polydimethyl siloxane soft segments. U.S. Patent 5,461,122, October 24, 1995.
- 31 Alberto Ballistreri, D. G., Mario Giuffrida, Giorgio Montaudo', Identification of the ions produced by fast atom bombardment mass spectrometry in some polyesters and polyamides. *Anal. Chem.* 1987, 59 (17), 2024-2027.
- 32 Vitalini, L. M. G. M. E. S. S. R. D., Organotin-Mediated Synthesis of Macrocyclic Tetraesters. A Combined IH NMR Spectroscopy, Gel Permeation Chromatography, and Fast Atom Bombardment Mass Spectrometry Approach to Complete Product Analysis. *Macromolecules* 1989 22 (8), 3275-3280.
- 33 Peponi, L.; Navarro-Baena, I.; Sonseca, A.; Gimenez, E.; Marcos-Fernandez, A.; Kenny, J. M., Synthesis and characterization of PCL–PLLA polyurethane with shape memory behavior. *Eur. Polym. J.* 2013, 49 (4), 893-903.
- 34 Besghini, D.; Mauri, M.; Simonutti, R., Time Domain NMR in Polymer Science: From the Laboratory to the Industry. *Appl. Sci.* 2019, 9 (9), 1801-1834.
- 35 Tian, M. K. S. Y. Y., Energy Gaps and their Control in Thiophene-Based Polymers and Oligomers. In *Handbook of Thiophene-based Materials: Applications in Organic Electronics and Photonics*; John Wiley & Sons, Ltd: New York, 2009; pp 341-364.
- 36 DFT calculations were performed under the level of (SMD)- M06/6-311++G(d,p)-SDD//B3LYP-D3(BJ)/6-31G(d,p)-SDD by Gaussian program. See SI for computational details.
- 37 Edward L. Marshall, V. C. G., Henry S. Rzepa, A Computational Analysis of the Ring-Opening Polymerization of rac -Lactide Initiated by Single-Site η^5 -Diketiminato Metal Complexes: Defining the Mechanistic Pathway and the Origin of Stereocontrol. *J. Am. Chem. Soc.* 2005, 127 (16), 6048-6051.
- 38 Jitonnom, J.; Molloy, R.; Punyodom, W.; Meelua, W., Theoretical studies on aluminum trialkoxide-initiated lactone ring-opening polymerizations: Roles of alkoxide substituent and monomer ring structure. *Comput. Theor. Chem.* 2016, 1097, 25-32.
- 39 Marlier, E. E.; Macaranas, J. A.; Marell, D. J.; Dunbar, C. R.; Johnson, M. A.; DePorre, Y.; Miranda, M. O.; Neisen, B. D.; Cramer, C. J.; Hillmyer, M. A.; Tolman, W. B., Mechanistic Studies of epsilon-Caprolactone Polymerization by (salen)AlOR Complexes and a Predictive Model for Cyclic Ester Polymerizations. *ACS Catal.* 2016, 6 (2), 1215-1224.
- 40 Wei, J.; Riffel, M. N.; Diaconescu, P. L., Redox Control of Aluminum Ring-Opening Polymerization: A Combined Experimental and DFT Investigation. *Macromolecules* 2017, 50 (5), 1847-1861.
- 41 Macaranas, J. A.; Luke, A. M.; Mandal, M.; Neisen, B. D.; Marell, D. J.; Cramer, C. J.; Tolman, W. B., Sterically Induced Ligand Framework Distortion Effects on Catalytic Cyclic Ester Polymerizations. *Inorg. Chem.* 2018, 57 (6), 3451-3457.
- 42 Mandal, M.; Luke, A. M.; Dereli, B.; Elwell, C. E.; Reineke, T. M.; Tolman, W. B.; Cramer, C. J., Computational Prediction and Experimental Verification of ϵ -Caprolactone Ring-Opening Polymerization Activity by an Aluminum Complex of an Indolide/Schiff-Base Ligand. *ACS Catal.* 2018, 9 (2), 885-889.
- 43 Sattayanon, C.; Kungwan, N.; Punyodom, W.; Meepowpan, P.; Jungsuttiwong, S., Theoretical investigation on the mechanism and kinetics of the ring-opening polymerization of epsilon-caprolactone initiated by tin(II) alkoxides. *J. Mol. Graphics Modell.* 2013, 19 (12), 5377-5385



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