Mechanism of Ring-Opening Polymerization of 1,5-Dioxepan-2-one and L-Lactide with Stannous 2-Ethylhexanoate. A Theoretical Study

Maria Ryner, Kajsa Stridsberg, and Ann-Christine Albertsson*

Department of Polymer Technology, Royal Institute of Technology, SE-100 44 Stockholm, Sweden

Henrik von Schenck and Mats Svensson*

Department of Materials Physics, Royal Institute of Technology, SE-100 44 Stockholm, Sweden, and Organic Chemistry, Royal Institute of Technology, SE-100 44 Stockholm, Sweden

Received December 8, 2000

ABSTRACT: A theoretical study of the ring-opening polymerization (ROP) mechanism of 1,5-dioxepan-2-one (DXO) and L-lactide (LLA) with stannous(II) 2-ethylhexanoate ($Sn(Oct)_2$) is presented. The B3LYP density functional method has been used for the quantum chemical calculations. Our results support a coordination−insertion mechanism initiated by a tin−alkoxide species formed prior to the ROP. The rate-determining step in the ROP was the nucleophilic attack of the alkoxide on the carbonyl carbon of the monomer. The activation energy for the ROP of DXO with $Sn(Oct')_2$ has been determined to be 19.8 kcal/mol and for L-lactide 20.6 kcal/mol. At normal reaction temperatures, a ligand may dissociate as Oct′H during propagation. An excess of carboxylic acid hinders the coordination of monomer to the initiating/propagating complex.

Introduction

Stannous(II) 2-ethylhexanoate ($Sn(Oct)_2$) is one of the most widely used compounds for initiating the ring-opening polymerization (ROP) of various lactones and lactides.[1−7] Despite thorough investigations and several mechanism proposals,[8−12] during more than 30 years of industrial use, both the ROP mechanism and the initiating complex remain unclear. $Sn(Oct)_2$ produces stereoregular polymers of high molecular weight in combination with high yields.[2,9,13] $Sn(Oct)_2$ can also catalyze transesterification reactions[10,13] of lactones and lactides. Consequently, the reaction mechanism is very difficult to determine by kinetic studies or from analysis of end groups and reaction products. It is also difficult to elucidate the structure of the actual initiating and propagating species of ROP by spectroscopic or chromatographic methods.

In the literature, two major ROP mechanisms are proposed: the activated monomer mechanism[10,11] and the coordination−insertion mechanism.[8,9,14−16] Both mechanisms are thought to be alcohol-initiated,[11,13,14,17,18] since the degree of polymerization is clearly dependent on the monomer-to-alcohol ratio,[19,20] and the end groups of the polymer have hydroxyl functionalities. The coordination−insertion mechanism provides an explanation of the highly stereoregular polymers obtained with $Sn(Oct)_2$.

In the activated monomer mechanism, $Sn(Oct)_2$ forms a donor−acceptor complex with a monomer. This activates the monomer toward alcohol attack. A hydroxyl-ended macromolecule attacks the carbonyl carbon and ring-opening proceeds. In the coordination−insertion mechanism, a compound containing a hydroxide group is believed to react with $Sn(Oct)_2$ to form the actual initiator, i.e., an alkoxide covalently bound to tin. A comparative study between two initiating systems, $Sn(Oct)_2$ with butanol and Sn(II) butoxide, shows that the growing polymer chain in these systems can be identical.[20] Recent investigations[16,19] on $Sn(Oct)_2$ systems have actually confirmed the presence of a tin−alkoxide complex by MALDI-TOF mass spectrometry. The reaction pathway proposed by Penzcek and co-workers involves the dissociation of at least one 2-ethylhexanoate group from the metal complex in the form of the corresponding acid. Recent studies by Kricheldorf and co-workers[21] support the dissociation of 2-ethylhexanoic acid. The presence of carboxylic acids decreases the reaction rate.[8,14] This effect has been proposed as a blocking of the coordination site or more recently explained as a shift in the equilibrium between $Sn(Oct)_2$ and Sn(Oct)−alkoxide species.[20]

This paper presents a theoretical study of the ROP mechanism of 1,5-dioxepan-2-one (DXO) and L-lactide initiated by $Sn(Oct)_2$ and methanol. The B3LYP method has been used to calculate the potential energy surface for the ROP mechanism. The ROP mechanism of L-lactide initiated by aluminum trialkoxides has recently been studied using semiempirical methods in combination with density functional methods.[22] Density functional methods has also been successfully used to investigate the mechanisms of olefin polymerization with metallocenes and late transition metal complexes.[23−26] The present work studies the coordination−insertion mechanism of DXO and L-lactide with $Sn(Oct)_2$. The experimental observations reported in the literature have been compared with the theoretical results to gain new insight into the ROP mechanism.

Computational Details

Geometries and energies of all intermediates were optimized using the hybrid density functional method B3LYP.[27] This popular and computationally relatively cheap method predicts reliable geometries and energetics.[28−38] A basis set of double-ζ valence quality labeled LANL2DZ was used in the Gaussian98 program.[39] A relativistic electron core potential (ECP) developed by Hay and Wadt replaced the Sn core electrons.[40,41] For nonmetal atoms, the double-ζ basis sets of Huzinaga and Dunning were assigned.[42,43] We

10.1021/ma002096n CCC: \$20.00

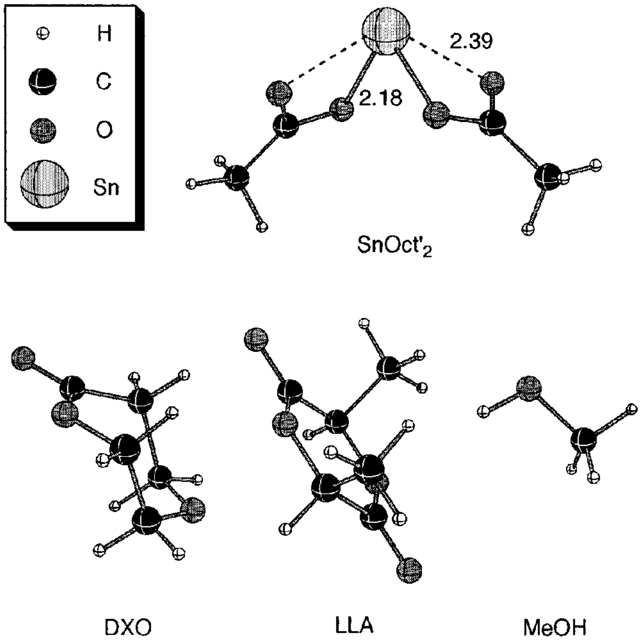

Figure 1. Structures of the reactants in the ROP systems. Distances are given in angstroms.

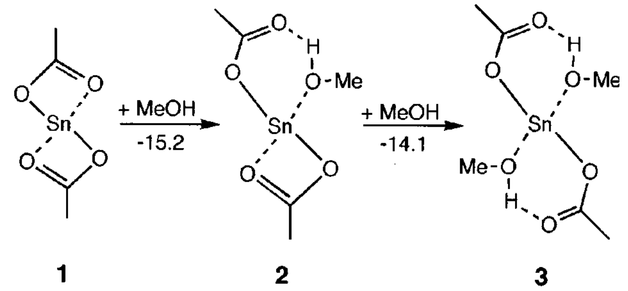

Figure 2. Hydroxyl functionalities coordinate to $Sn(Oct')_2$ prior to the ring-opening sequence. Hydrogen bonding between the alcohols and the Oct′ ligands contributes to the coordination strength. Energies are given in kcal/mol.

Table 1. Energies (kcal/mol) of the Intermediates and Transition States in the ROP of DXO and LLA, Relative to Structure 4

entry	structure	energy[a]	energy[b]	energy[c]
1	**3**	3.3	3.8	8.8
2	**4**	0.0	0.0	0.0
3	**TS45**	19.8	20.6	16.1
4	**5**	11.2	6.8	7.4
5	**TS56**	15.0	24.8	11.1
6	**6**	−8.5	−10.0	−3.4

[a] Reacting species are DXO and $Sn(Oct')_2(MeOH)_2$. [b] Reacting species are LLA and $Sn(Oct')_2(MeOH)_2$. [c] Reacting species are DXO and MeOSnOct′(MeOH).

recalculated all energies using a triple-ζ contracted basis set at the B3LYP level, i.e., the 6-311G(d,p) basis set[44,45] for all nonmetal atoms, and a 3s3p contraction of the Hay and Wadt primitive basis set for Sn augmented with one d-function (0.18).[46] The character of all intermediates and transition states was checked by frequency calculations.

Results and Discussion

The Initiating System and Stable Structures. The systems modeled in this study are the ring-opening polymerizations of 1,5-dioxepan-2-one (DXO) and L-lactide with stannous(II) 2-ethylhexanoate ($Sn(Oct)_2$) and methanol as the initiating complex. In the calculations, the $Sn(Oct)_2$ structure was somewhat modified to cut computational costs. The 2-ethylhexanoate ligands were replaced by acetoxy groups (Oct′); i.e., the structural elements that are nonessential for the mechanistic understanding of the reaction were removed. Methanol was used to represent both the initiating hydroxyl functionality and the propagating polymer chain. All components of the polymerization system are shown in Figure 1.

The calculations confirmed that the carboxylate ligands (Oct′) have a bidental coordination to tin.[17] The coordination of the acyl oxygen to tin was stronger than the coordination of the carbonyl oxygen, as indicated by the shorter bond length (see Figure 1). A characteristic property of the $Sn(Oct)_2$ was its pyramidal geometry. This structure was favored over the planar structure by 17.6 kcal/mol.

Formation of the Active Species. A stable complex was formed with alcohol coordinating to $Sn(Oct')_2$ prior to the actual ring-opening sequence (Figure 2).

The first step involved coordination of methanol to **1** ($Sn(Oct')_2$) to form structure **2**. As the alcohol coordinated to tin (the Sn−O bond is 2.21 Å), a hydrogen bond was simultaneously formed to the carbonyl oxygen atom of the Oct′ ligand. The enthalpy of coordination was −15.2 kcal/mol for methanol. A second alcohol coordinated to **2** to form structure **3**, with an enthalpy of coordination of −14.1 kcal/mol. Similar results were also obtained in calculations carried out with water or more sterically demanding alcohols like benzyl alcohol.[47] Kricheldorf et al. have experimentally observed the rapid complexation of benzyl alcohol to $SnOct_2$ by ^{1}H NMR and ^{119}Sn NMR.[9]

The Coordination−Insertion Mechanism. The coordination−insertion mechanism involving the ROP of DXO with $Sn(Oct')_2$ is presented in Figure 3. The ROP of L-lactide with $Sn(Oct')_2$ is not presented since the mechanistic pathway is equivalent to the DXO/ $Sn(Oct')_2$ system. The relative energies of all the structures in the two systems are given in Table 1.

The initial step involved the weak complexation of monomer to complex **3**. The enthalpies of coordination were −3.3 and −3.8 kcal/mol for DXO and LLA, respectively. Although weak, coordination of the monomer had an important influence on the chemical nature of the ligand structure. Proton migration was induced from the alcohol to the nearby Oct′ ligand. Consequently, the Oct′ ligand took on the character of a carboxylic acid, while the alcohol was converted into an alkoxy-type species. The Sn−O bond distances changed from 2.15 to 2.10 Å for the methoxy group and from 2.26 to 2.59 Å for the Oct′H ligand. The O−H distances changed from 1.08 to 1.28 Å for the methoxy group and from 1.40 to 1.14 Å for the Oct′ ligand. The ligand retained its acid character throughout steps **4** to **TS56**, stabilizing these structures through hydrogen bonding. After precursor **4** was formed, the methoxy group performed a nucleophilic attack on the monomer's carbonyl carbon, and a new C−O bond was formed between monomer and methoxy group via the four-center transition state **TS45**. The activation energy of the step was 19.8 kcal/mol, which was almost identical to the equivalent step in the LLA polymerization (20.6 kcal/mol). The rate-determining step in the ROP proved to be this C−O bond formation for both monomers. The experimental reaction barrier for ROP of LLA has been reported to be 17 ± 0.4 kcal/

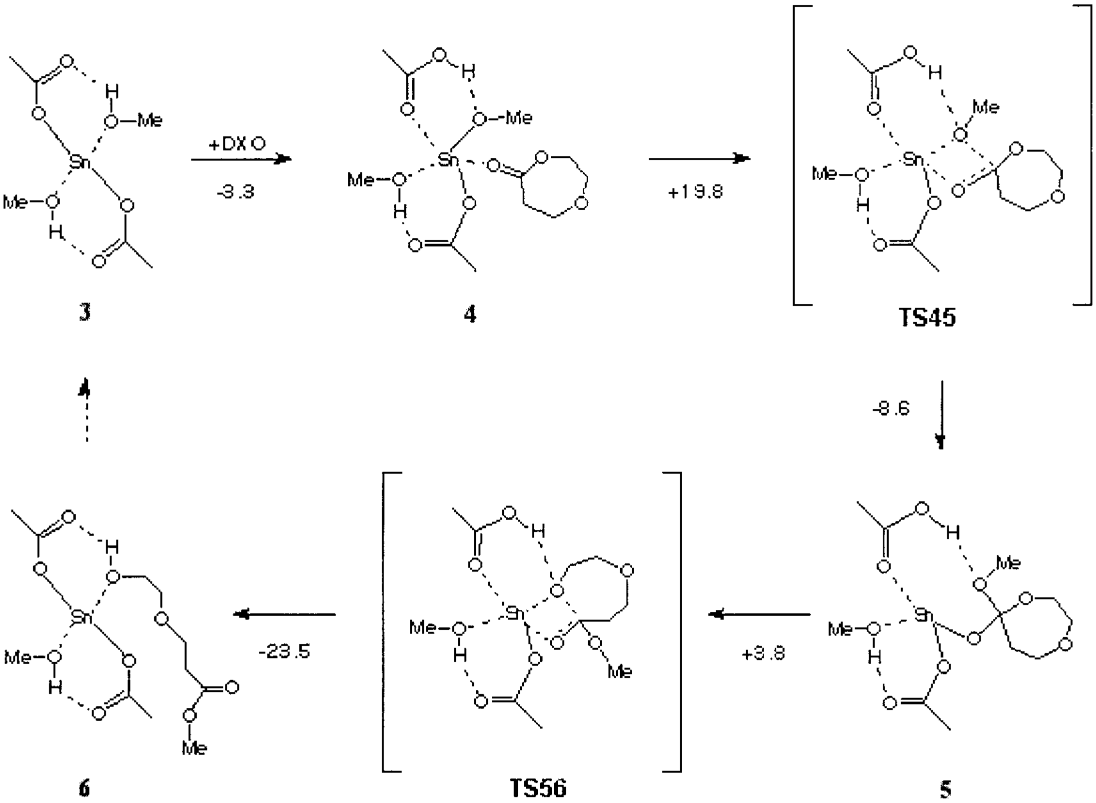

Figure 3. Mechanism of ring-opening polymerization of DXO with Sn(Oct′)$_2$. Step **4** to **TS45** is the rate-determining step in the sequence. Energies are given in kcal/mol.

mol,[48] in good agreement with our theoretical values. The step from **4** to **5** was endothermic by 11.2 and 6.8 kcal/mol for DXO and LLA, respectively. This difference can be explained by the greater accessibility of the π^*-LUMO in the LLA monomer, located at the carbonyl carbon, which leads to a more stable intermediate structure.[49] The next step in the mechanism was the actual ring-opening of the monomer, **5** to **6**. In the intermediate **5**, the former carbonyl oxygen is coordinated to tin via an alkoxide bond, and the carbonyl carbon adopts an sp^3 bonding geometry.

This arrangement allows for rotation around the C−O axis and enables the endocyclic oxygen to rotate into position for ring-opening. **TS56** was once again a four-center transition state, structurally analogous to **TS45**, although the bonds formed in **TS56** were the bonds broken in **TS45**, and vice versa. This can be seen in the bond lengths in Figure 4.

The activation energy for step **5** to **6** was only 3.8 kcal/mol for DXO but 18.0 kcal/mol in the case of LLA. This difference can tentatively be explained as being due to several contributing factors. First, the driving force from intermediate **5** to the product **6** was greater for DXO, i.e., 2.9 kcal/mol more exothermic. Furthermore, the stability of **TS56** is probably influenced sterically by the methyl substituents on LLA and by the greater strain in the six-membered ring than in the seven-membered DXO ring during the ring-opening process. The initiation as well as the propagation cycle was completed with formation of **6**, the analogue to species **3**. To reach the stable structure **6**, a hydrogen transfer has occurred. The Oct′H ligand has thus reverted to its original Oct′ structure, and the polymer chain coordinated to tin has regained its hydroxyl functionality.

An important parallel reaction to the ring-opening of monomer is the reversible chain transfer process[19] between the propagating chain and the hydroxyl-terminated polymer chains in the system in principle, the step from **6** to **3**. The enthalpy of coordination for the ring-opened product in structure **6** was −13.2 kcal/mol, which is similar to the coordination strength of methanol, water, and benzyl alcohol. The coordination energy provides an estimate of the barrier of polymer chain exchange, assuming a dissociative mechanism. Since the ring-opening barrier was approximately 20 kcal/mol, chain transfer is extensive in the system. Furthermore, the extensive chain transfer agrees with the relatively narrow molecular weight distribution observed in these systems.

The Role of Carboxylic Acids. The addition of a carboxylic acid, e.g., octanoic acid, significantly decreases the rate of polymerization.[8,17,18] This may be explained by a blocking of the active coordination site[14] or a shift in equilibrium between different tin complexes.[20] Our calculations confirm a site-blocking effect. Displacing the DXO monomer in complex **4** with Oct′H was favored by 7.9 kcal/mol.

A perhaps more intriguing behavior of octanoic acid is found with a Oct:Sn ratio ≤ 2:1. It has been observed experimentally that Sn(Oct)$_2$ contains a small fraction of the dissociated and protonated ligand, 2-ethylhexanoic acid (OctH).[8] Furthermore, Penczek and coworkers[19,20] suggested that the Oct ligands actually dissociate as OctH, prior to the ROP. To further investigate the role of OctH in the propagation cycle, calculations were performed on the DXO/Sn(Oct′)$_2$ system after removing one ligand as Oct′H. The intermediates and transition states were analogues to those presented in Figure 3. Removing the protonated Oct′ ligand from the tin−alkoxide complex gives the appropriate structures. The relative energies for these structures are given in Table 1.

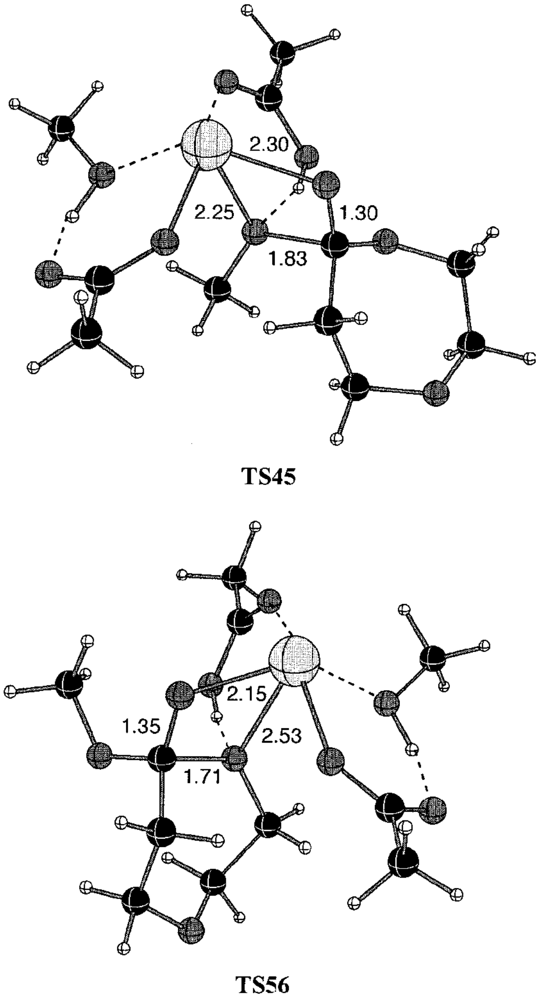

Figure 4. Transition state structures in the ring-opening polymerization of DXO with $Sn(Oct')_2$. Distances are given in angstroms.

The reaction barriers (equivalent to step **4** to **TS45** and step **5** to **TS56**) are lowered if Oct′H is removed. Specifically, the activation barrier of the rate-determining step was lowered from 19.8 to 16.1 kcal/mol. These calculations agree well with the recently reported experimental results on the polymerization of L-lactide with different ratios of $Sn(OBu)_2$ to OctH.[20,50] At Oct:Sn ratios less than 2:1, the polymerization of L-lactide proceeds extremely rapidly.

At this point it is relevant to discuss whether the acid is coordinated to tin during the propagation. The enthalpy of dissociation of Oct′H from precursor **4** was 14.2 kcal/mol. Typical entropy values (ΔS) for a dissociative reaction, $A \rightarrow B + C$, at room temperature correspond to an energy of the order of −8 kcal/mol.[51,52] The reaction barrier can thus be estimated to be 22 kcal/mol, which can be compared to 19.8 kcal/mol in the case where no acid dissociates from **4**. This implies that the acid could dissociate from the tin−alkoxide complex during ROP at normal reaction temperatures (100−130 °C).

Conclusions

The ROP of DXO and LLA with $Sn(Oct')_2$ has been studied using density functional methods. The reaction proceeds via a coordination−insertion mechanism initiated by a tin−alkoxide complex formed prior to initiation. The activation barriers were 19.8 kcal/mol for DXO and 20.6 kcal/mol for LLA. The mechanism predicts facile (reversible) chain transfer in the system, and this explains the relatively narrow molecular weight distribution obtained.

Octanoic acid can dissociate during propagation at normal reaction temperatures (100−130 °C). An excess of carboxylic acid in the system hinders coordination of the monomer to the tin−alkoxide complex.

Acknowledgment. We thank the Swedish Research Council for Engineering Sciences, TFR, diary no 210, project: kemiteknik 1999-658 and the Swedish Natural Science Research Council, NFR, for financial support. We also thank the Ernst Johnson foundation for a scholarship. We gratefully acknowledge Parallelldatorcentrum at the Royal Institute of Technology for providing the computer facilities.

References and Notes

(1) Gilding, D. K.; Reed, A. M. *Polymer* **1979**, *20*, 1459−1464.
(2) Dahlmann, J.; Rafler, G.; Fechner, K.; Mehlis, B. *Br. Polym. J.* **1990**, *23*, 235−240.
(3) Grijpma, D. W.; Zondervan, G. J.; Pennings, A. J. *Polym. Bull.* **1991**, *25*, 327−333.
(4) Kricheldorf, H. R.; Meier-Haack, J. *Makromol. Chem.* **1993**, *194*, 715−725.
(5) Albertsson, A.-C.; Löfgren, A. *J. Macromol. Sci., Pure Appl. Chem.* **1995**, *A32*, 41−59.
(6) Albertsson, A.-C.; Gruvegård, M. *Polymer* **1995**, *36*, 1009−1016.
(7) Albertsson, A.-C.; Palmgren, R. *J. Macromol. Sci., Pure Appl. Chem.* **1993**, *A30*, 919−931.
(8) Kowalski, A.; Duda, A.; Penczek, S. *Macromol. Rapid Commun.* **1998**, *19*, 567−572.
(9) Kricheldorf, H. R.; Kreiser-Saunders, I.; Boettcher, C. *Polymer* **1995**, *36*, 1253−1259.
(10) In't Veld, P. J. A.; Velner, E. M.; van de Witte, P.; Hamhuis, J.; Dijkstra, P. J.; Feijen, J. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 219−226.
(11) Du, Y. J.; Lemstra, P. J.; Nijenhuis, A. J.; van Aert, H. A. M.; Bastiaansen, C. *Macromolecules* **1995**, *28*, 2124−2132.
(12) Schwach, G.; Coudane, J.; Engel, R.; Vert, M. *J. Polym. Chem.* **1997**, *35*, 3431−3440.
(13) Schindler, A.; Hibionada, Y. M.; Pitt, C. G. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 319−326.
(14) Zhang, X.; Macdonald, D. A.; Goosen, M. F. A.; Mcauley, K. B. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 2965−2970.
(15) Kricheldorf, H. R.; Stricker, A. *Macromol. Chem. Phys.* **2000**, *201*, 2557−2567.
(16) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **2000**, *33*, 7359−7370.
(17) Nijenhuis, A. J.; Grijpma, D. W.; Pennings, A. J. *Macromolecules* **1992**, *25*, 6419−6424.
(18) Storey, R. F.; Taylor, A. E. *J. Macromol. Sci., Pure Appl. Chem.* **1998**, *A35*, 723−750.
(19) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **2000**, *33*, 689−695.
(20) Duda, A.; Penczek, S.; Kowalski, A.; Libiszowski, *J. Macromol. Symp.* **2000**, *153*, 41−53.
(21) Kricheldorf, H. R.; Kreiser-Saunders, I.; Stricker, A. *Macromolecules* **2000**, *33*, 702−709.
(22) Eguiburu, J. L.; Fernandez-Berridi, M. J.; Cossio, F. P.; San Román, J. *Macromolecules* **1999**, *32*, 8252−8258.
(23) Yoshida, T.; Koga, N.; Morokuma, K. *Organometallics* **1996**, *15*, 766.
(24) Lohrenz, J. C. W.; Woo, T. K.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 12793.
(25) Musaev, D. G.; Froese, R. D. J.; Svensson, M.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 367.
(26) Deng, L.; Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 1094.
(27) Stevens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
(28) Musaev, D. G.; Morokuma, K. *J. Phys. Chem.* **1996**, *100*, 6509.
(29) Erikson, L. A.; Pettersson, L. G. M.; Siegbahn, P. E. M.; Wahlgren, U. *J. Chem. Phys.* **1995**, *102*, 872.

(30) Ricca, A.; Bauschlicher, Jr., C. W. *J. Phys. Chem.* **1994**, *98*, 12899.

(31) Heinemann, C.; Hertwig, R. H.; Wesendrup, R.; Koch, W.; Schwarz, H. *J. Am. Chem. Soc.* **1995**, *117*, 495.

(32) Hertwig, R. H.; Hrusak, J.; Schröder, D.; Koch, W.; Schwarz, H. *Chem. Phys. Lett.* **1995**, *236*, 194.

(33) Schröder, D.; Hrusak, J.; Hertwig, R. H.; Koch, W.; Schwerdtfeger, P.; Schwarz, H. *Organometallics.* **1995**, *14*, 312.

(34) Fiedler, A.; Schröder, D.; Shaik, S.; Schwarz, H. *J. Am. Chem. Soc.* **1994**, *116*, 10734.

(35) Fan, L.; Ziegler, T. *J. Chem. Phys.* **1991**, *95*, 7401.

(36) Berces, A.; Ziegler, T.; Fan, L. *J. Phys. Chem.* **1994**, *98*, 1584.

(37) Lyne, P. D.; Mingos, D. M. P.; Ziegler, T.; Downs, A. J. *Inorg. Chem.* **1993**, *32*, 4785.

(38) Li, J.; Schreckenbach, G.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 486.

(39) Gaussian 98, Revision A.3: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.

(40) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(41) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

(42) Dunning Jr., T. M. *J. Chem. Phys.* **1971**, *55*, 716.

(43) Dunning Jr., T. M. *J. Chem. Phys.* **1970**, *53*, 2823.

(44) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(45) Krishnan, R.; Binkley, R. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(46) Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111.

(47) Water coordinates to $Sn(Oct')_2$ with a strength of 14.4 kcal/mol. Benzyl alcohol coordinates to $Sn(Oct')_2$ with a strength of 14.8 kcal/mol.

(48) Witzke, D. R.; Narayan, R.; Kolstad, J. J. *Macromolecules* **1997**, *30*, 7075−7085.

(49) The difference in orbital energies for the LUMO of DXO and LLA was calculated to be 0.73 eV.

(50) Kowalski, A.; Libiszowski, J.; Duda, A.; Penczek, S. *Macromolecules* **2000**, *33*, 1964−1971.

(51) Page, M. I., Williams, A., Eds.; *Enzyme Mechanics*; The Royal Chemical Society: Burlington House, London, 1987; p 6.

(52) McClelland, *Statistical Thermodynamics*; Chapman and Hall: New York, 1982; p 266.

MA002096N