



# Environment-friendly transesterification to seawater-degradable polymers expanded: Computational construction guide to breaking points

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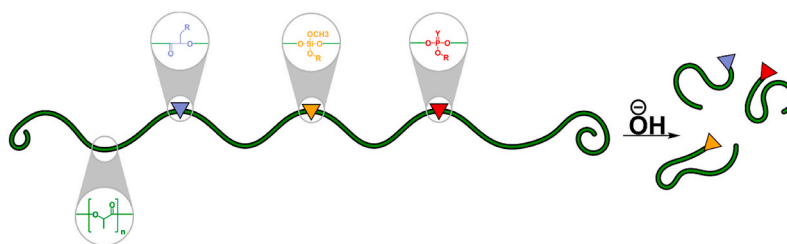
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## HIGHLIGHTS

- Simulation of degradation of polylactide derivatives with specially designed breaking points.
- Influence of breaking points structure on polymer stability.
- All phosphoester-based breaking points degraded by an intramolecular RNA-inspired transesterification.
- Precise control over the degradation of polylactide by the structure of breaking points.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Marine plastic pollution caused by non-biodegradable polymers is a major worldwide concern. So-called “biodegradable” polymers should reduce plastic pollution in the environment by the safeguard of biodegradation. However, many polyesters degrade very slowly in seawater. We therefore designed a systematic library of “breaking points” that are installed into a polylactide backbone and simulated their degradation mechanisms, including internal and external  $S_N2$  mechanisms, Addition-Elimination (AE) mechanisms, and RNA-inspired mechanisms. The breaking points are composed of phosphoesters with pendant nucleophiles directly at the P-atom, or structurally similar silicones, or side-chain functional polyesters. All P-containing breaking points react via the RNA-inspired mechanism, while Si-containing linkers undergo decomposition via the A-E mechanism. For C-containing linkers, only when a long pendant chain (4 carbon atoms) is present can the reaction proceed via the RNA-inspired mechanism. In cases of shorter pendants, the Addition-Elimination (AE) mechanism is energetically favorable. We believe that these calculations will pave the way for the synthesis of exceptionally seawater-degradable polyesters in the future that can act as a safeguard to prevent microplastic formation after eventual littering.

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## 1. Introduction

Controlling the degradation of polymers is important to prevent the formation of microplastics in the environment. This is especially crucial as several million tons of plastic waste are entering the oceans every year (Thushari and Senevirathna, 2020; Wang et al., 2021). Several polymers, mainly polyesters, are summarized under the label “biodegradable polymers” (Luckachan and Pillai, 2011); however, their degradation rates differ strongly depending on the environmental conditions (Haider et al., 2019). While polylactide, a common “biodegradable polymer”, degrades in reasonable times *in vivo* (for biomedical applications) or during the composting of packaging (Haider et al., 2019; Ulery et al., 2011), almost no degradation occurs in seawater for several years (Bagheri et al., 2017). The successful use of computational guidance for installing phosphoester “breaking points” into polylactide (PLA) and polyethylene-like polymers allows us to accelerate and control the degradation rates in aqueous conditions as present in seawater (Haider et al., 2021; Rheinberger et al., 2021). The strategy relies on an intramolecular transesterification of a pendant 2-hydroxy ethoxy group with the central phosphate linkage. Inspired by these initial results, herein we expand the scope of the “breaking points” by computer simulations to predict which other chemistries might be interesting to synthesize and evaluate in real environments, e.g. to design especially seawater-degradable polymers (Wang et al., 2021). Such materials might also be interesting for biomedical applications in drug delivery or tissue engineering (Ulery et al., 2011).

Our initial studies concentrated on phosphorus-containing spacers to mimic nature-inspired cyclization that occurs in RNA. The proposed RNA-inspired intramolecular transesterification mechanism was investigated experimentally (Haider et al., 2021; Rheinberger et al., 2021) and successfully modeled theoretically. In both cases, it has been shown that the RNA-inspired reaction pathway (left panels of Fig. 1) was energetically favored over hydroxyl group internal or external  $S_N2(P)$ , addition-elimination (AE), or intermolecular degradation mechanisms. A previous study by the group of Almutairi presented PLA-like polymers carrying nucleophilic side chains that resulted in accelerated backbone degradation, proposing an intramolecular transesterification

mechanism (Olejniczak et al., 2015). Motivated by these findings, we expand this approach theoretically and guide our future synthetic strategies to different breaking points, especially to understand if phosphorus is needed to control degradation rates in seawater. With phosphorus being a limited resource and to prevent eutrophication (Oliveira and Machado, 2013), phosphorus-free analogs might be particularly interesting, which have not been synthesized to date. To guide our syntheses in the lab we simulated various potential chemical structures of breaking points by the design of i) chemically different pendant chains relying on phosphorus in the polymer backbone and ii) different breaking points omitting the use of phosphorus. We believe that by covering computationally several possible mechanisms for a diverse number of pendant/linker combinations we will be able to design novel degradable polymers with a tailored degradation pattern.

## 2. Computational methods

All results reported herein have been obtained at the  $\omega$ B97X-D/def2-TZVP level of theory (Chai and Gordon-Head, 2008; Weigend and Ahlrichs, 2005) with the inclusion of the IEFPCM(SMD) continuum solvent model (Marenich et al., 2009) for aqueous solution. Protonation states or proton transfer processes, appropriate for seawater’s pH conditions have been considered; with their mildly basic character, hydroxyl and thionyl groups were considered deprotonated while amine groups were considered neutral (although alternative protonation states have also been tested). Mechanisms with internal or external hydroxyl group attack, as well as addition/elimination and cyclization/decomposition have been considered. All stationary points have been identified by Hessian analysis to be either energy minima (all real vibrational frequencies) or first-order saddle points (exactly one imaginary frequency). The nature of the identified transition states has been confirmed by either IRC procedure (Maeda et al., 2015) or (in simple cases) visualization. All calculations have been carried out using the Gaussian16 package (Frisch et al., 2016) while preparation/analysis/visualization of files has been performed using the GaussView6 program (Dennington et al., 2019).

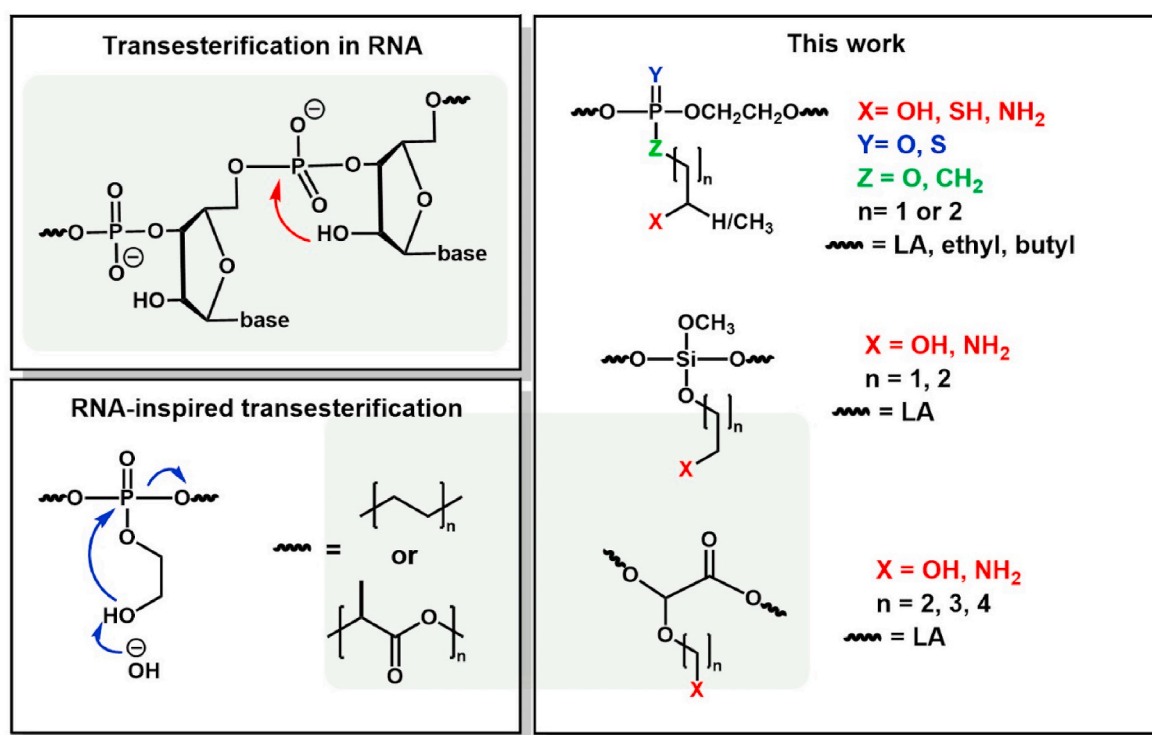


Fig. 1. RNA-inspired reactant (bottom left panels) and combinations of linker/pendant fragments used in the present studies (LA = lactide).

### 3. Results

In the studies presented herein, we have considered several mechanistic alternatives, including internal and external  $S_N2$  mechanisms, Addition-Elimination (AE) mechanisms, and RNA-inspired mechanisms. The qualitative energetics, based on our previously published results (Haider et al., 2021; Rheinberger et al., 2021) are presented in Fig. 2, which also illustrates the terminology used throughout this contribution. In all studied cases both variants of the  $S_N2$  mechanism were either more energy demanding than the alternative RNA-inspired or Addition-Elimination (AE) mechanisms, or else the transition states were not identified, and thus we limit further discussion to these two mechanisms. Furthermore, intermolecular degradation, as well as mechanisms in which the hydroxyl group of the pendant remained protonated, turned out to be energy-disfavored compared to either AE or RNA-inspired mechanisms and are therefore also excluded from further discussion.

Throughout this article we use the symbols depicted in Fig. 2 to refer to local minima and transition states (TS) of the reaction pathways of the considered mechanisms. Initial polymeric substrate (S) undergoes hydroxyl attack in  $S_N2$  or AE mechanisms. The first one leads directly to products while the second is a stepwise process in which hydroxylation leads to an intermediate ( $A^-$ ) that decomposes to products (P). Alternative mechanisms (and RNA-inspired) proceed with the initial deprotonation of the hydroxyl (or sulfuryl) group of the pendant ( $S^-$ ) which then attacks the central atom of the linker (P, C, or Si) to form the products directly ( $S_Ni$  mechanism) or via a cyclic intermediate (RNA-inspired mechanism).

#### 3.1. Phosphorus-based breaking points

In addition to the case involving models of lactate (single monomer or four monomers on each side) discussed in detail previously and the polyethylene model (four monomers on each side) (Haider et al., 2021; Rheinberger et al., 2021), herein we studied variants of these models that include thiono modification of the linker, as well as thio, amino, *sec*-hydroxyl, and phosphonate modifications of the pendant. The schematic representation of AE and RNA-inspired mechanisms for these models is provided in Fig. 3.

We have previously calibrated theoretical calculations on the experimental data (Rheinberger et al., 2021). Good agreement obtained between the calculations and experiments indicated that the reactions suitable for practical application should be characterized by a Gibbs energy of activation of about  $10 \pm 2$  kcal/mol (see Section 4. for details). Consequently, we considered mechanisms with overall barriers in the range of 8–12 kcal/mol. The energetics of suitable pendant/linker

combinations are presented in Fig. 4. In the legend, the part preceding the hyphen describes the pendant length, while the part after the hyphen describes the heteroatom at its end. The isopropyl pendant is indicated by the presence of the methyl group in the first part of the label. Furthermore, the thiono linker ( $Y=S$ ) and the results for the model with four monomers on each side (LA4) are also indicated in this part. The energetics represented by the black line correspond to the case communicated previously and can be considered as the reference point. All cases in which dotted lines have been used correspond to cases in which the RNA-inspired mechanism is favored energetically, while the one with dashed lines corresponds to the most favorable AE mechanism. In phosphorus-containing cases, this situation occurs only when the pendant contains the  $NH_2$  group. Its energetics (for C2) are included only for comparison (and highlighted by the dashed line) as its energy barrier is much too high to be used in practice. Also, the results for branched pendant ( $C2(CH_3)$ ) are provided only for comparison as an example of a reaction with a too-small energy barrier.

#### 3.2. Phosphorus-free breaking points

In all calculations, models included a single lactic monomer on each side of the linker that contained a pendant fragment expected to perform an intramolecular attack leading to the break in the polymer chain. The linker motifs were selected based on their feasibility of synthesis and potential for practical use in industry. In our previous synthetic study, we showed that for up to a few percent of breaking points included in a polylactide (PLA) backbone the mechanical and thermal properties did not change significantly. Three different motifs have been considered. The first one is the phosphate/phosphonate moiety discussed above. In the second motif, the phosphorus moiety has been changed to a silicon-containing one, while in the third to a carbon atom with a neighboring carbonyl group. For these two motifs, four pendant substituents, including the terminal  $NH_2$  group have been considered. The linker/pendant combinations used in the calculations and associated chemical steps in AE and RNA-inspired mechanisms are illustrated schematically in Fig. 5 and Fig. 6, respectively.

As in the case of phosphorus-based linkers, we have considered several possible mechanisms. As in the previous case, the only two yielding results within the appropriate energy window were AE and RNA-inspired mechanisms, although in the present cases, opposite to the results presented in Fig. 4, suitable energetics were obtained mostly with the AE mechanisms. The energy diagrams for reactions fulfilling the energy requirements are collected in Fig. 7.

### 4. Discussion

We have applied computational methods to consider numerous mechanistic possibilities for several linker/pendant combinations. Due to still numerous deficiencies of practical levels of theory, we believe that it is safer to first validate calculations on known reactions before applying them as a predictive tool for new reactions. With this aim in mind, we have thoroughly studied the mechanism of breaking the polymer chain in polylactide-based polymers with phosphoester breaking points. As reported in our recent communication (Rheinberger et al., 2021), an excellent agreement between calculations at the  $\omega$ B97X-D/def2-TZVP level of theory, with the inclusion of IE FPCM (SMD) continuum solvent model, and experimental results has been observed. Furthermore, with a recent report on studies of around 12,000 organic reactions at this theory level (Grambow et al., 2020), it can be considered the standard for the theoretical approach to chemical reactivity. We have therefore used this theory level to predict the reactivity of several reactions in search of a linker/pendant combination that improves properties regarding depolymerization conditions and at the same time environment friendliness.

Herein, we constrain the discussion only to reaction pathways that promise to be useful for practical use. Since our calculations agreed well

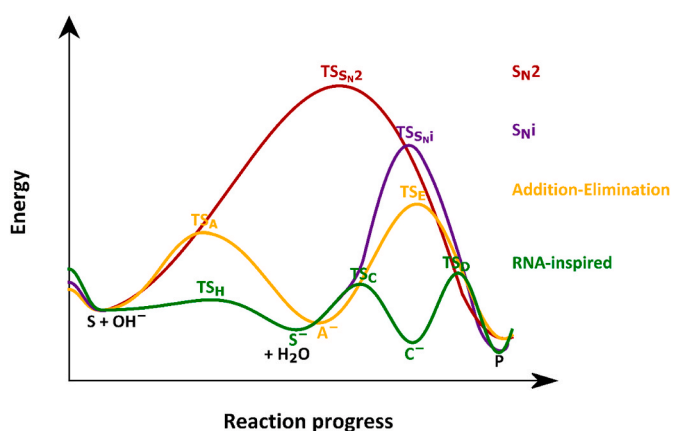
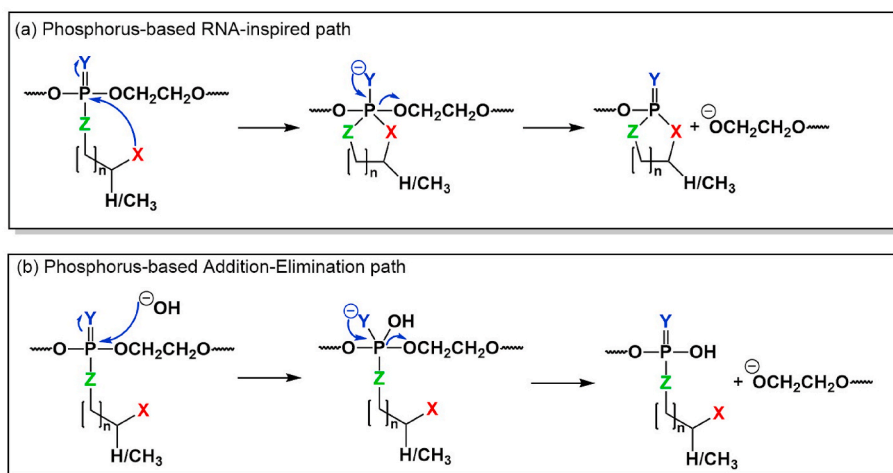
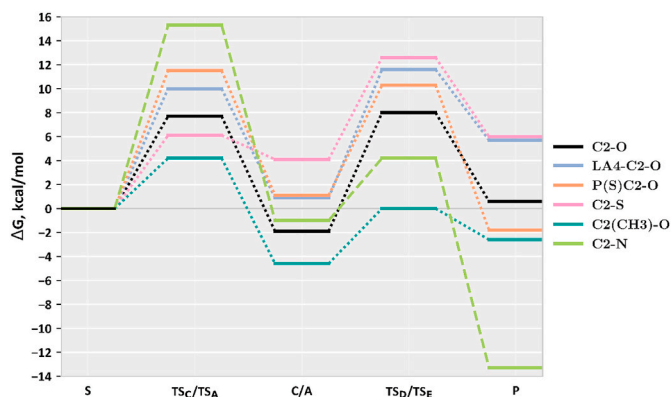


Fig. 2. Major alternative mechanisms considered, and the terminology used for the identification of stationary points on the reaction paths of different mechanisms.



**Fig. 3.** RNA-inspired (a) and Addition-Elimination (b) mechanisms for polymers with phosphorus-containing breaking points. X = OH, SH, or NH<sub>2</sub>, Z = O or CH<sub>2</sub>, Y = O or S, n = 1 or 2.

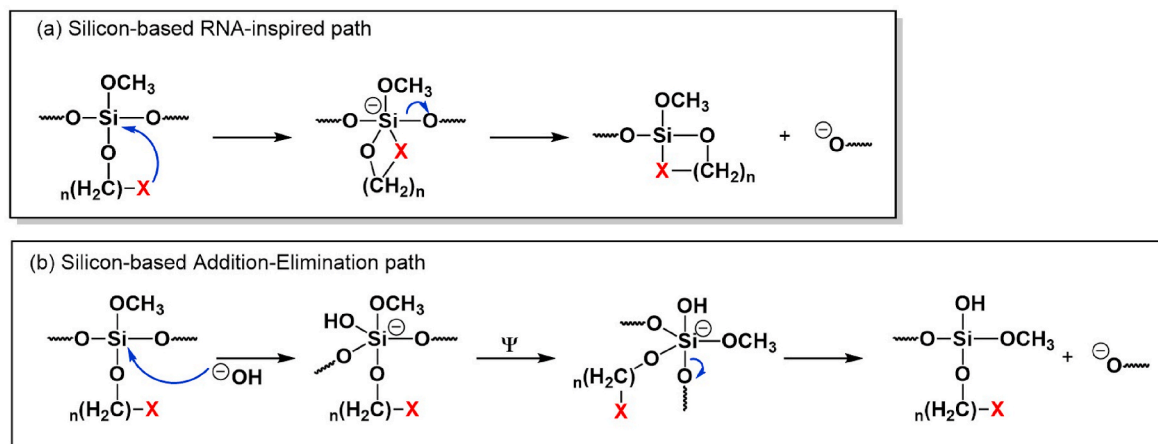


**Fig. 4.** Relative energetics of phosphorus-based models. See Section 3.1 for the explanation of the legend. Dotted lines indicate RNA-inspired mechanisms. Dashed lines indicate AE mechanisms (included for comparison only as it is outside the considered energy window).

with the experimental studies involving the phosphate linker, and since they are in the reasonable range, we conclude that reasonable systems should be characterized by energetic barriers of about 10 kcal/mol. However, based on variations of the computational results due to the use

of the continuum solvent model and thus possible inaccuracies in hydrogen bonding, as well as noticeable energy differences between rotamers and stereoisomers which amount to about 2 kcal/mol, we estimate that the systems that are worth considering should have the overall barriers within the 8–12 kcal/mol range. Higher energy barriers would render basic hydrolysis not efficient enough, while too low barriers would lead to materials that are not sufficiently stable for practical applications.

From the considered library of PLA-derivatives with phosphoester breaking points, four systems fulfill this restriction. Their energetic profiles are illustrated in Fig. 4 and highlighted by the dotted lines connecting the energy levels of individual reactants. They contain two carbon atoms in the pendant group carrying either an OH or SH group as the nucleophile - in all these cases, the RNA-inspired mechanism is energetically favored. The obtained values are relatively invariant to the length and kind of the polymer used in calculations as well as thiono (Y=S) and thiol (X=SH) modifications. On the contrary, the length and type of pendant can significantly diminish the barrier for the dissociation of the cyclic intermediate, while changing the primary hydroxyl group in the pendant chain to a secondary one causes a significant lowering of the barrier to cyclization. The barriers for the phosphonate type of pendant group (i.e. with a P-C-bond) and the one with secondary OH (the latter rendered in green in Fig. 4 and included only for comparison) are so low (6.3 and 4.6 kcal/mol, respectively) that such a



**Fig. 5.** RNA-inspired (a) and Addition-Elimination (b) mechanisms for polymers with silicon-containing breaking points. X = OH, or NH<sub>2</sub>, and n = 2 or 3. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

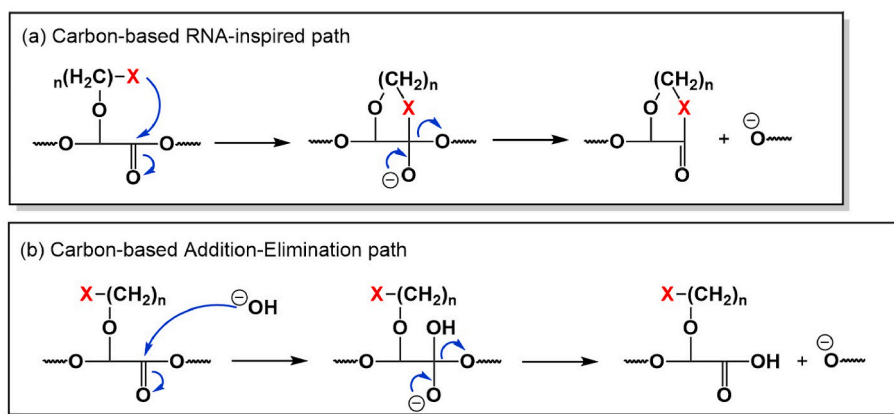


Fig. 6. RNA-inspired (a) and Addition-Elimination (b) mechanisms for polymers with carbon-containing breaking points. X = OH, SH, or NH<sub>2</sub>, and n = 2, 3 or 4.

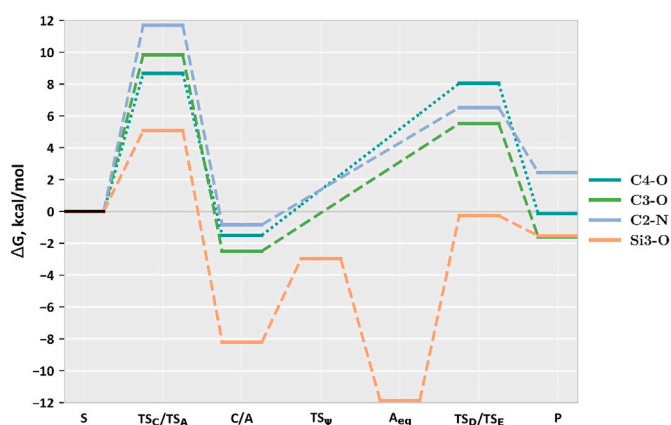


Fig. 7. Relative energetics of phosphorus-free models. Dotted lines indicate RNA-inspired mechanism while dashed lines indicate AE mechanism.

material would not be useful for practical applications as it would decompose too fast. The results obtained for pendant groups containing an NH<sub>2</sub>-group are also outside the assumed energy window (labeled by aquamarine lines) and are provided only for comparison. These reactions proceed by the AE mechanisms with a rate-determining addition step requiring about 16 kcal/mol.

Although we have expanded the arsenal of phosphorus-containing compounds, in this contribution we have concentrated mostly on the results of the search for other combinations of breaking points in PLA that would result in suitable kinetic parameters that would not release phosphate into the environment. Among the combinations of breaking points and pendant groups that are within the assumed acceptable energy range, there are three systems with carbon-based linkers and one

with silicon-based linker, all with the dominating AE mechanism. In the latter case, the rate-determining step is the decomposition step with a Gibbs free energy of activation of 11.6 kcal/mol that follows pseudorotation of the intermediate. In comparison to the “reference” reaction studied experimentally, our calculations indicate that the best choices for practical use should be those that contain a carbon-based linker and hydroxyl group with either three (C3–O) or four (C4–O) carbon atoms in the pendant group. The first one reacts via the AE mechanism with the rate-determining step being the external hydroxyl anion attack that leads to the formation of the adduct. The energy barrier of this step is 9.8 kcal/mol, while the barrier of the subsequent elimination step is only 6.8 kcal/mol. Elongation of the pendant to four atoms results in a change of the energetically favored mechanism from AE to RNA-inspired. In this case, the Gibbs free energy of activation of the cyclization step is 8.7 kcal/mol, while the rate-determining step is the subsequent dissociation with the barrier of 9.6 kcal/mol. Rate-controlling barriers in both these cases are very close to the 9.9 kcal/mol found for the reference reaction. Structures of transition states of rate-limiting steps are illustrated in Fig. 8.

## 5. Conclusions

The ability to reliably predict the mechanism and kinetic properties of a given reaction or a class of reactions allows the saving of time and resources and thus can immensely improve the design of new materials. Herein, we have studied computationally polylactide-derivatives with specially designed breaking points that should guarantee biodegradation in seawater. Inserts contained either phosphorus-, carbon-, or silicon-based breaking points with a pendant group of different lengths and nucleophile groups. Our findings lead to the following conclusions:

- All P-containing breaking points react via the RNA-inspired mechanism. In these cases, an OH-group in the secondary position or lack of

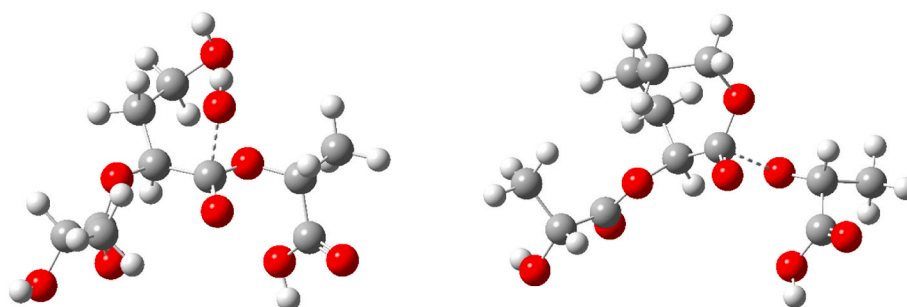


Fig. 8. Transition state structures for the slowest (rate-controlling) step of reactions worth pursuing experimentally. TS<sub>A</sub> for C3–O (left) and TS<sub>D</sub> for C4–O (right). Forming/breaking bonds are rendered with dashed lines.

oxygen in the pendant (phosphonate) leads to substantial lowering of the barriers to the point, which probably prevents practical application.

- Si-containing linkers all undergo decomposition via the AE mechanism with the slowest step being pseudorotation of the intermediate. Energetics of these reactions, however, are mostly outside the acceptable range.
- In the case of C-containing linkers, only when a long pendant chain (4 carbon atoms) is present does the reaction proceed via the RNA-inspired mechanism. In the cases of shorter pendants, the Addition-Elimination (AE) mechanism is energetically favorable.
- The calculations performed indicate that the carbon-based linkers with the pendants containing 3–4 carbon atoms and hydroxyl groups are the best candidates for experimental studies.

### Authors' contributions

Conceptualization and Methodology, P.P., A.P. F.R.W.; Calculations and Data Curation, M.R., P.P., T.R.; Original Draft Preparation, P.P., A. P.; Draft revision: all authors; Funding acquisition, P.P., F.R.W.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request.

### Acknowledgments

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