

¹ Graphical Abstract

² **Computational study of the glycolytic degradation of poly(ethylene tereph-**
³ **thalate catalyzed by N^1,N^2 -bis(2-aminobenzyl)-1,2-diaminoethane zinc (II)**

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6 Highlights

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11 • Research highlight 1

12 • Research highlight 2

13 Computational study of the glycolytic degradation of
14 poly(ethylene terephthalate catalyzed by
15 N^1,N^2 -bis(2-aminobenzyl)-1,2-diaminoethane zinc (II)

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18 **Abstract**

A possible reaction mechanism of the glycolytic degradation of poly(ethylene terephthalate) (PET) catalyzed with N^1,N^2 -bis(2-aminobenzyl)-1,2-diaminoethane zinc (II) (ABEN) was determined using Kohn-Sham density functional theory (KS-DFT) using the range-separated hybrid, generalized gradient approximation functional, ω -B97X-V with DFT-D4 dispersion correction [1] using def2-TZVPP over the zinc, oxygen and nitrogen atoms and def2-SVP for the rest, Making use of an energy-weighted climbing image nudged elastic band (EW-CI-NEB) algorithm [2] to determine the minimum energy path (MEP) and then optimizing the converged climbing image (CI) using eigenvector-following partitioned rational function optimization (EF P-RFO) to obtain the transition state (TS). The non-covalent interactions were obtained using an averaged independent gradient model (aIGM) algorithm [3]

19 *Keywords:*

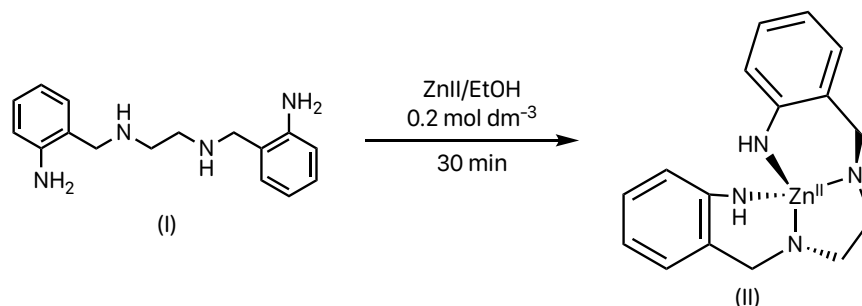
20 KS-DFT, Polymer degradation, Catalysis

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1. Introduction

By 2015, the annual global production of plastics surpassed 367 million tonnes; 55 % of all plastic waste was discarded, 25.5 % incinerated and just 19.5 % was recycled [4]. Poly(ethylene terephthalate) (PET) is one of the most widely traded polymer there is on the market. It's mainly used in the fabrication of bottles, packages and fibers. The widespread usage of this plastic is due to its properties, like an excellent tensile strength, chemical resistance, clarity, processability and a reasonable thermal stability, It is also very cheap to produce [5, 6]. Albeit all its properties, PET is also becoming a global problem, since a lot of it is not recycled at all. It is becoming a waste problem. Even though PET by itself is not harmful to humans and by itself does not impose an environmental damage, because of its substantial presence in bodies of water and its high resistance to biological and atmospheric agents, PET is classified as a nocive material [7] Chemical recycling of PET has become an important topic since this is the most sustainable way of recycling plastic, and produces *de novo* the starting materials of the synthesis of PET. There is an extensive amount of literature on the topic of chemical degradation of PET, processes such as methanolysis, hydrolysis and glycolysis have been thoroughly studied [8–10]. The most sustainable reaction of degradation of PET is the glycolysis since this reaction produces Bis(2-hydroxyethyl) terephthalate (BHET), one of the precursors of PET itself. PET glycolysis, nevertheless is not a very effective process if no catalyst is used. Plenty of studies have been made on the reaction of the degradation of PET via catalyzed glycolysis. Some transition metals such as zinc lead to a good yield in this type of reactions with the benefit that zinc is not a very toxic metal. For the chemical recycling of PET, numerous protocols involving hydrolysis, methanolysis and glycolysis among many others [8–10]



Scheme 1: Reported synthesis of ABEN [13]. The structure of ABEN (II) was derived from the electronic structure computations obtained in this study.

have been reported. The uncatalyzed glycolysis of PET is not an effective process; transition metal (TM) salts have been determined to aid in this reaction. The oldest report of the catalyzed glycolytic degradation of PET was reported by Vaidya and Nadkarni [11] in which they carried the reaction using different metal acetates as catalysts. Then it was determined that Zn^{II} has a great in comparison to other TM (Mn^{II} , Co^{II} and Pb^{II}) activity as a catalyst in the glycolysis of PET [12]. Alongside the numerous zinc catalysts studied to date, a novel zinc catalyst, N^1, N^2 -bis(2-aminobenzyl)-1,2-diaminoethane zinc(II) (ABEN) [13] has shown to have a great catalytic activity in the glycolytic degradation of PET yielding around 78 % of BHET[14]. The main purpose of this article is to evaluate the possible reaction mechanism involved in this catalyzed glycolytic depolymerization of PET with ABEN and determine the covalent or non-covalent interactions involved.[15, 16]

2. Experimental

2.1. Computational details

The software ORCA 5.0.2 [17] was used to perform all the geometry optimizations, single point energy, energy-weighted climbing image nudged elastic band

63 followed by transition state optimization (NEB-TS) and multidimensional relaxed
64 surface scans. For all of the geometry optimizations and vibrational analysis, the
65 meta-generalized-gradient approximation (mGGA) functional r^2 SCAN-3c which
66 uses the dispersion correction DFT-D4 [18] was used; and for all the single point
67 energy and NEB-TS computations, the range-separated hybrid, generalized gradi-
68 ent approximation functional, ω -B97X-V with DFT-D4 dispersion correction was
69 employed.¹

70 2.2. Modeling of the intermediates

71 The starting configurations for EG and ABEN were defined and pre-optimized
72 using XTB, [19] with the force field GFN2-xTB [20]. After this crude pre-optimization
73 a conformational and rotamer search was done using CREST [21] In the case of
74 ABEN just one configuration was possible. For EG, six of the lowest energy con-
75 formers were re-optimized as described in 2.1 and the lowest in energy was used
76 for this study. The starting configuration for DBHET was proposed using crystallo-
77 graphic data for PET [22] and extending the unit cell to two units, then re-optimizing
78 this coordinates using r^2 SCAN-3c def2/TZVP.

79 2.3. NEB-TS method to elucidate the glycolysis mechanisms

80 The optimized structures were then merged onto the same Cartesian coordi-
81 nates and then re-optimized in r^2 SCAN-3c def2/SVP. Then, a multidimensional
82 relaxed surface scan was performed keeping constrained, and varying the bond
83 distances in 20 steps to obtain the products of the reactions depicted in . The opti-
84 mized product and the starting geometry of the relaxed surface scan where the input

¹Unless otherwise stated, all computations were made using basis set (BS) def2-SVP with def2-TZVPP over the zinc, oxygen and nitrogen atoms and using def2/J as an auxiliary BS.

85 for an Energy-Weighted Climbing image Nudged Elastic Band (EW-CI-NEB) [2]
86 algorithm to find the path of minimum energy connecting both ends, followed by
87 a P-RFO optimization to find a TS performed onto the climbing image (CI).

88 In order to determine covalent and non-covalent interactions regions between
89 the molecules, an analysis based on Hirshfeld partition of molecular density (IGMH)
90 algorithm within multiwfn was performed [23] onto the optimized reactant. To
91 minimize computation time, aIGM was performed with the MEP obtained by
92 NEB-TS.

93 With JANPA [24], CLPOs and bond orders for the reactants, products and
94 transition states were obtained.

95 3. Results

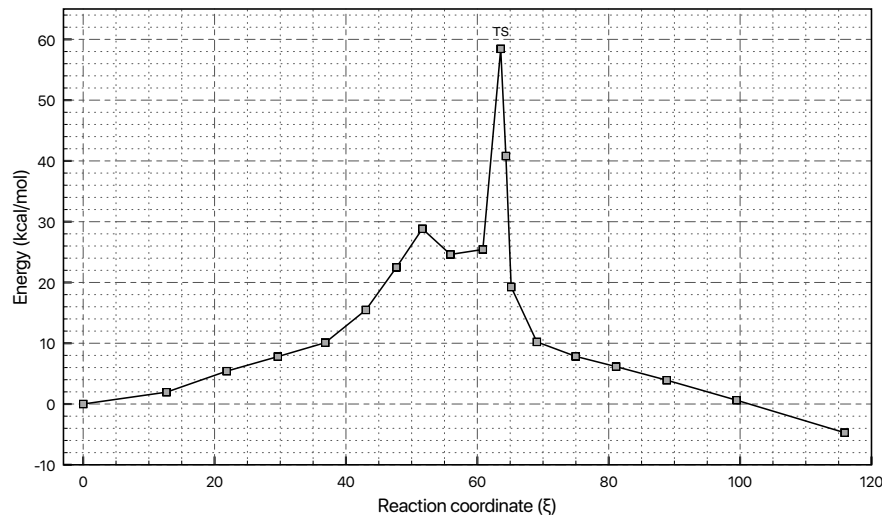


Figure 1: Minimum energy path obtained by NEB-TS on the uncatalyzed system.

96 **4. Discussion**

97 **5. Conclusion**

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