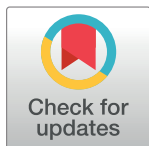RESEARCH ARTICLE

Chemical reactivity theory to analyze possible toxicity of microplastics: Polyethylene and polyester as examples

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Abstract

Micro- and nanoplastics are widespread throughout the world. In particular, polyethylene (PE) and polyethylene terephthalate or polyester (PET) are two of the most common polymers, used as plastic bags and textiles. To analyze the toxicity of these two polymers, oligomers with different numbers of units were used as models. The use of oligomers as polymeric templates has been used previously with success. We started with the monomer and continued with different oligomers until the chain length was greater than two nm. According to the results of quantum chemistry, PET is a better oxidant than PE, since it is a better electron acceptor. Additionally, PET has negatively charged oxygen atoms and can promote stronger interactions than PE with other molecules. We found that PET forms stable complexes and can dissociate the guanine-cytosine nucleobase pair. This could affect DNA replication. These preliminary theoretical results may help elucidate the potential harm of micro- and nanoplastics.

Introduction

Microplastics (< 5 mm in size) and nanoplastics (< 100 nm diameter) come from fragmentation of plastic particles through biological (metabolism), chemical (oxidation or hydrolysis) and physical degradation (UV interaction, mechanical processes) [1–6]. Micro- and nanoplastics are consumed by humans and animals. Previous research suggests that humans ingest an amount of plastics equivalent to one credit card per year [7, 8]. Micro- and nanoplastics are everywhere, but the question is whether they are really toxic.

There are many studies to determine possible danger of plastics in the environment and animal life [9–27]. Some indicate a relationship with oxidative stress. Others report that microplastics are ingested and evacuated without producing biochemical changes [22]. Recent investigations with Positron Emission Tomography to visualize biodistribution of radioplastics in mice reveal that most radioplastics remain in the gastrointestinal tract and, after 48 hours of consumption, they are eliminated through the feces [24]. While there is information for

humans and also for other species, all experiments reported so far used large concentrations of nanoplastics to test the effects [14]. The problem is that these concentrations cannot occur in the environment. Long-term exposure of environmental amounts is needed to understand the toxicity of nanoplastics in humans and other organisms. With all the information reported so far, the damage that micro- and nanoplastics can cause in humans or animals is still uncertain.
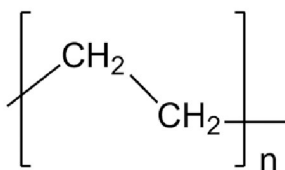
Polyethylene is the most common and cost-effective polymer, used as plastic bags and films [28–31]. Many kinds of polyethylene are known [28], with most having the chemical formula $(C_2H_4)_n$. The most common polyester is polyethylene terephthalate (PET). This has been extensively used in textiles. The demand of PET is increasing due to the extreme "use and waste" economy of clothing, promoted many times by fashion [29–31]. PET is also one of the most common polymers identified in samples of drinking water [11]. Nano- and microplastics of polyester and polyethylene could be dangerous.

Despite all the information we have about micro- and nanoplastics in different environments and about the effect that these particles can have on health, there is a lot of uncertainty about their harmful properties. There is also no theoretical research on potential toxicity of these polymers. There are some publications on molecular simulations to determine the effect of nanometric polystyrene particles [32] and the theory of chemical reactivity has been used to study the environmental risk [33–35] of different substances. There are also studies on oxidative stress and nanoplastics [36–39] but there are not theoretical studies on oxidative stress or the direct interactions of nanoplastics with DNA nitrogen bases. For this reason, the main idea of this investigation is to theoretically study different oligomers as models of polyethylene and polyester (polyethylene terephthalate, PET) using Density Functional Theory and different chemical reactivity indices (see Fig 1 for molecular formulas). Since polymers are difficult to optimize, oligomers with different numbers of units are used as models for polyethylene and polyester. Oligomers as models of polymers have been used previously with success [40, 41]. The results of this research can help to understand possible health effects of micro- and nanoplastics, and may determine which of these two plastics is potentially more dangerous.

Computational details

Gaussian09 was used for all electronic calculations [42]. Geometry optimizations of initial geometries were obtained at M062x/6-311g+(2d, p) level of theory without symmetry constraints [43–45]. Harmonic analyses verified local minima (zero imaginary frequencies). Conceptual Density Functional Theory is a chemical reactivity theory founded on Density Functional Theory based concepts [46–53]. Within this theory there are response functions such as the electro-donating (ω-) and electro-accepting (ω+) powers, previously reported by

polyehtilene (PE)   polyethylene terephthalate (PET)
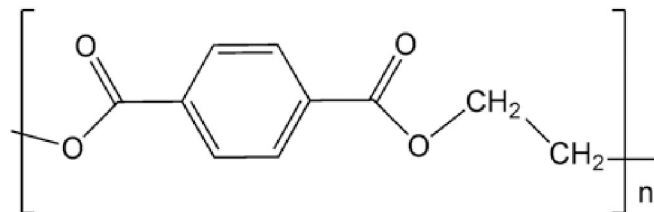

Fig 1. Schematic representation of PE and PET.

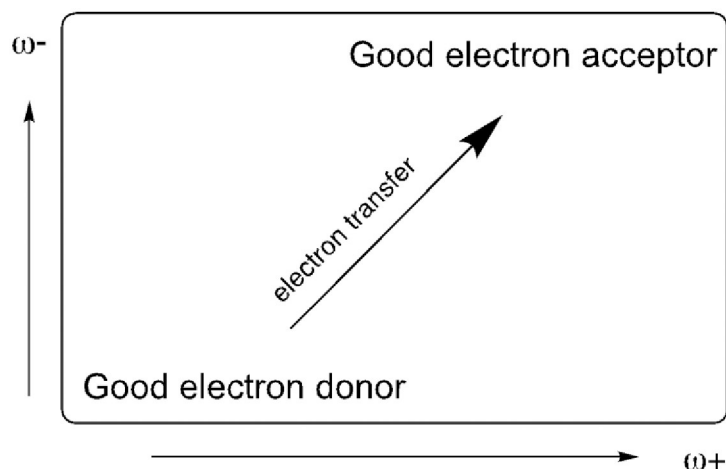https://doi.org/10.1371/journal.pone.0285515.g001

Fig 2. Electron Donor-Acceptor Map (DAM).

Gázquez *et al*. [48, 49] The propensity to donate electrons or ω- is defined as follows:

$$\omega- = (3I + A)^2/16(I - A) \qquad (1)$$

whereas the propensity to accept electrons or ω+ is equal to

$$\omega+ = (I + 3A)^2/16(I - A) \qquad (2)$$

I and A are vertical ionization energy and vertical electron affinity, respectively. They are obtained as follows:

$$A \rightarrow A^{+1} + 1e \quad I = E(A^{+1}) - E(A) \qquad (3)$$

$$A^{-1} \rightarrow A + 1e \quad A = E(A) - E(A^{-1}) \qquad (4)$$

Lower values of ω- indicate good electron donor molecules. Higher values of ω+ are for good electron acceptor molecules. ω- and ω+ refer to charge transfers, not necessarily from one electron. With these parameters it is possible to determine the Electron Donor-Acceptor Map (DAM, see Fig 2) [54]. Systems located down to the left are considered good electron donors whilst those situated up to the right are good electron acceptors. It can expect that electrons will be transferred from molecules considered good electron donors to those considered good electron acceptors. These chemical descriptors have been used successfully in many different chemical systems [55–59].

Results and discussion

Different oligomers of polyester and polyethylene are used as models to investigate the electronic characteristics of polymers-like structures. This approach was previously used with success to study conducting polymers [40, 41]. Polymer biodegradation consists of several steps that break down large polymers to form the monomer, and then the monomer is mineralized to carbon dioxide and water [6, 60, 61]. Therefore, it is important to know the electronic properties as the size of the system decreases. For this reason, we started from the monomer and continued with different oligomers until the chain length was greater than 2 nm. In Figs 3 and
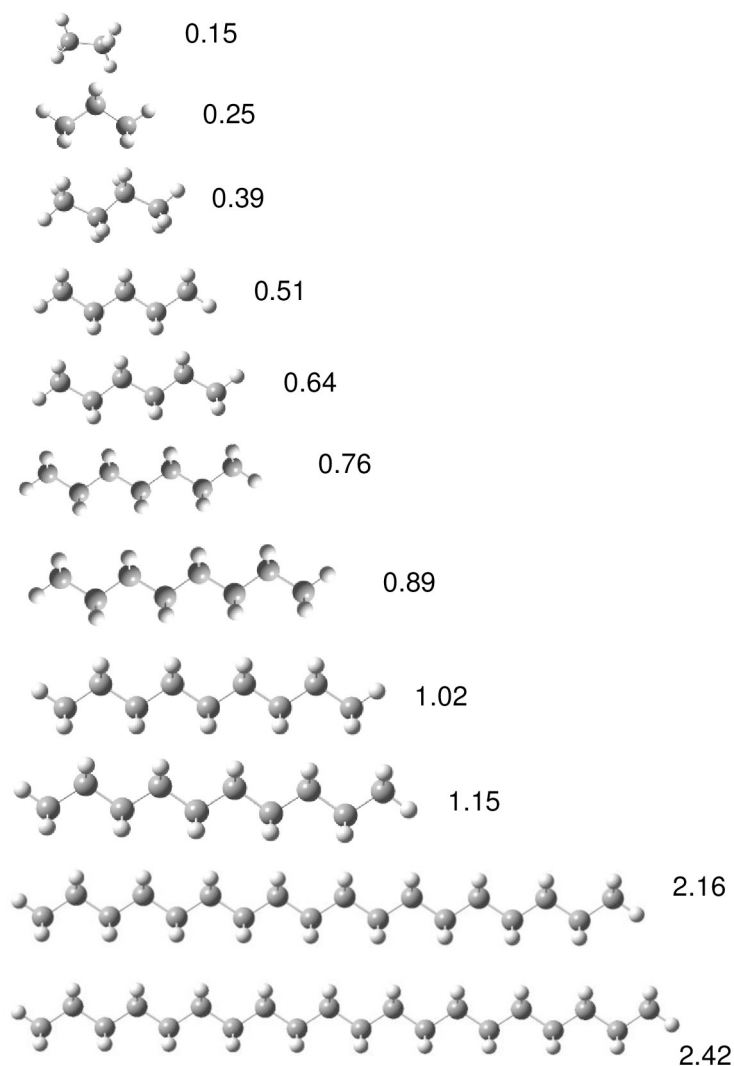
Fig 3. Optimized structure of different models of polyethylene (PE). Numbers represent chain length in nm.

4 the optimized structures of the models that investigated are shown. The correspondent length of the oligomer is also reported.

To investigate possible oxidative stress caused by micro- and nanoplastics, electro-donating and electro-accepting powers of all the systems under study were calculated. Good electron acceptors will take electrons from other systems. Good electron donors will donate electrons. The DAM for these oligomers is reported in Fig 5. Systems located down to the left are good electron donors. Therefore, they donate electrons producing the reduction of other molecules that gain these electrons. Systems located up the right are good electron acceptor. They accept electrons, oxidizing other species.

The results of Fig 5 show interesting patterns. For oligomers of polyethylene, the ability to donate and also the ability to accept electrons decreases as the size of the system increases. They become more reductant molecules and probably they are not capable of oxidizing other systems. For PET's oligomers the results are similar. The ability to accept or donate electrons of the three systems is different and there is also a correspondence with the size of the
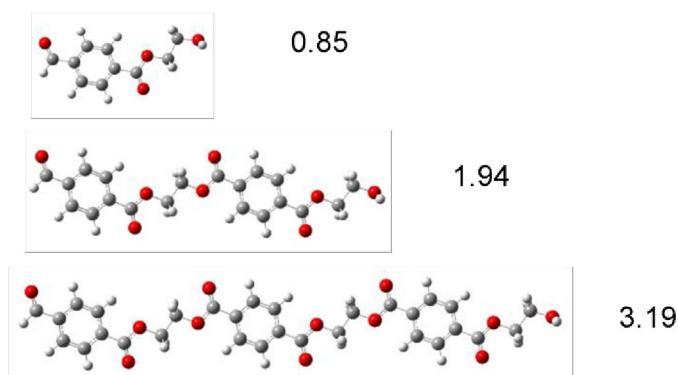
Fig 4. Optimized structure of different models of polyester (PET). Numbers represent chain length in nm.

oligomer. The bigger the system, the better electron acceptor it will be. They are located at the top right, so they are better electron acceptors and worse electron donors than the polyethylene´s oligomers. This result is as expected, since the electron affinity of oxygen is greater than that of carbon. The more oxygen atoms the molecule has, the better electron acceptor it will be. This means that PET´s oligomers are better oxidants than those of polyethylene and may produce oxidative stress oxidizing other molecules. Polyethylene´s oligomers are better electron donors and they may reduce other molecules. To investigate the importance of being a good oxidant or good reductant, it is necessary to compare with molecules of interest, as nucleobases.

To investigate the capability of oligomers to interact with nucleobases through electron transfer processes, we optimized geometries of adenine, thymine, cytosine and guanin, and we calculated the electron transfer properties. Adenine-thymine and cytosine-guanine pairs are
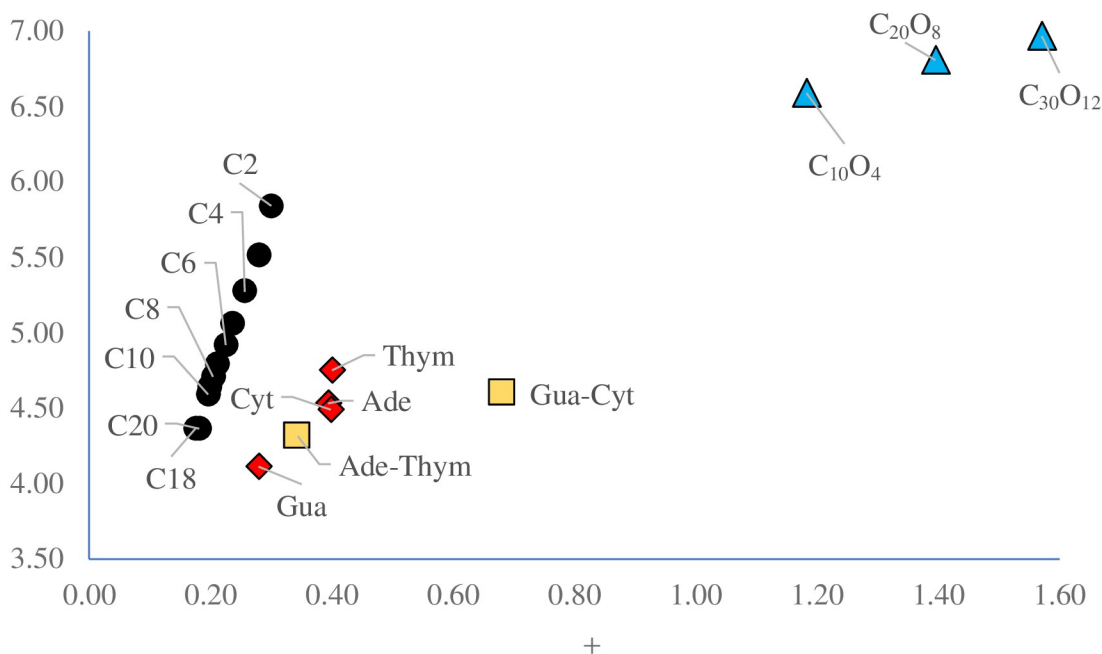

Fig 5. DAM of system under study. Values in eV.

also investigated. In order to compare the electron donor acceptor capacity of all systems. Results are reported in Fig 5. All nucleobases are located down to the left in the DAM. They are good electron donors and poor electron acceptors. Comparing with polyethylene´s oligomers, it can be seen that both are ubicated in the same region of the DAM. Electron donor capability is quite similar, being nucleobases slightly better electron acceptors. Therefore, no electron transfer is expected between polyethylene and nucleobases. With polyester the results are different. Nucleobases are located down to the left of the PET´s oligomers and electron transfer from nucleobases to these oligomers could be possible. Polyester can oxidize nucleobases and therefore, microplastics of PET can be harmful. More investigations are needed to corroborate this idea.

In vivo uptake and transport of nanoplastics depend on their own structure and properties, such as chemical composition [62]. Due to the differences in electronegativity of C and O, negative atomic charge in oxygen and carbon atoms can be anticipated. Mulliken Atomic Charges of $C_{18}H_{38}$ and $C_{20}H_{18}O_8$ as models of both nanoplastics corroborate this idea (see Fig 6). All oxygen atoms of PET oligomer are negatively charged whilst polyethylene oligomer presents negative carbon atoms. One possible risk of nanoplastics in the body is the interaction with important biomolecules as nucleobases for example. Both oligomers can form hydrogen bonds with nucleobases. PET can interact via oxygen atoms, while polyethylene can form hydrogen bonds with hydrogen atoms, since the carbons are sterically less accessible. The atomic charge of the hydrogens of polyethylene´s oligomer is smaller than the atomic charge of the oxygen atoms of PET´s oligomer. Stronger hydrogen bonds are expected with PET than with polyethylene.

To corroborate this idea and analyze possible harmful effects of nanoplastics, we investigated interactions of nucleobases with oligomers of polyethylene or polyester. The dissociation energies of X-guanine and X-guanine-cytosine (X is oligomers of polyethylene or PET) are analyzed to mimic possible interactions with DNA. The interactions of nanoplastics´ oligomers and guanine or guanine-cytosine base pair allow us to investigate possible effects of nanoplastics on these two nucleobases that are bonded in DNA. We used oligomers of
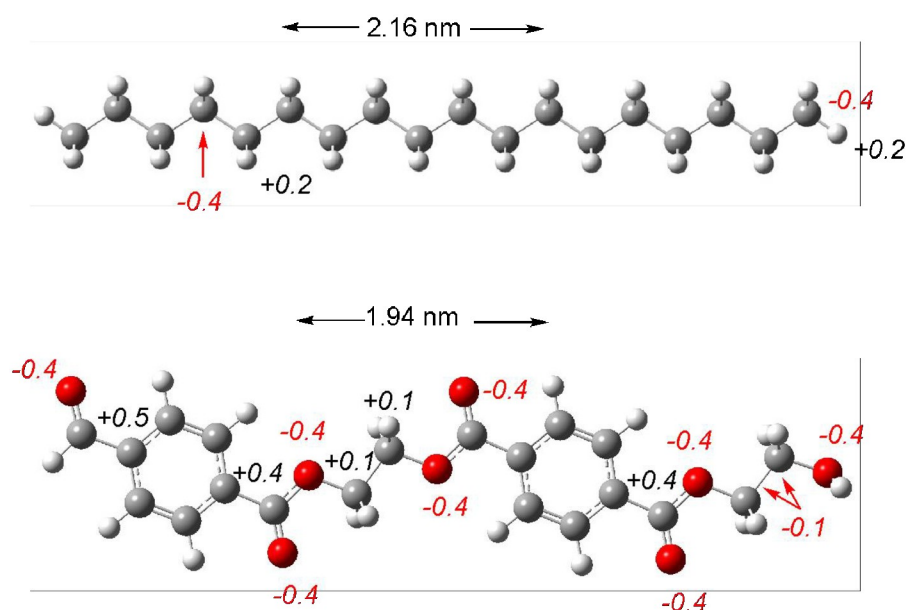

Fig 6. Mulliken atomic charges of $C_{18}H_{38}$ and $C_{20}H_{18}O_8$.

polyethylene and polyester, with ten and twenty carbon atoms respectively. Dissociation energies are calculated considering guanine or guanine-cytosine as products and following Eqs 5 and 6.

$$E_{dis} = \{[E(X) + E(guanine)] - E(X - guanine)\} \qquad (5)$$

$$E_{dis} = \{[E(X) + E(guanine - cytosine)] - E(X - guanine - cytosine)\} \qquad (6)$$

X is oligomers of polyethylene or PET. The results are reported in Fig 7. It is possible to see that different hydrogen bonds are formed. With polyethylene, the N and O of guanine form hydrogen bonds, with bond length of 2.2 to 2.8 Å. The hydrogen atoms of polyethylene form H-H bonds with cytosine and there is also one hydrogen bond with the oxygen atom of cytosine. The bond length of hydrogen bonds of cytosine is 2.0–2.6 Å. All PET- guanine and PET-guanine-cytosine hydrogen bonds are with an oxygen atom, either from PET, guanine or cytosine. The bond length of these hydrogen bonds is 2.0 to 2.3 Å. These results corroborate the idea that arises from the Mulliken atomic charges. Hydrogen atoms of polyethylene and oxygen atoms of PET form hydrogen bonds. As expected, oxygen atoms of guanine and cytosine also form hydrogen bonds with H atoms of polyethylene or PET. Due to the bond distance, it is expected that hydrogen bonds of nucleobases with PET are stronger than those of nucleobases with polyethylene. This conclusion is also obtained from the dissociation energies. Negative dissociation energies represent stable dissociated systems. Complexes with polyethylene´s oligomers are less stable than the dissociated system, *i.e.* stable complexes are not formed. With guanine, the binding energy is small (4.2 kcal/mol) and within the limits of the calculations, so the formation of a stable compound cannot be considered. For PET´s oligomers, the dissociation energy is positive and the complexes are more stable than the dissociated structures. PET's oligomer interacts with guanine, forming a 12.3 kcal more stable complex than the dissociated system. PET-guanine-cytosine complex is more stable than the dissociated system by 21.3 kcal/mol.

This could be related with the toxicity of micro- and nanoplastics. PET could be more dangerous than polyethylene since the interaction of correspondent oligomers with nucleobases is more stable for the first than for the second. Polyester forms stable complexes and can promote the dissociation of guanine-cytosine pairs. This possible interaction may be related to the toxicity of nanoplastics made from polyester. Polyethylene is expected to be less dangerous since the interaction with guanine and guanine-cytosine pair is not stable, so these nanoplastics will not interfere with DNA replication.

Conclusions

Micro- and nanoplastics have long-term stability under environmental conditions, an important factor that increases the potential for living organisms to be exposed to these materials. So far, no clear toxic effects of micro and nano- have been observed. Based on the results reported here, it is possible to state that PET can be expected to be more harmful than PE for three reasons: PET is better electron acceptor and therefore a better oxidant than polyethylene; PET has negatively charged oxygen atoms and can promote stronger interactions than PE with other molecules; PET forms stable complexes and can dissociate the guanine-cytosine nucleobase pair. These first results contribute to understand potential dangerous of these two microplastics.
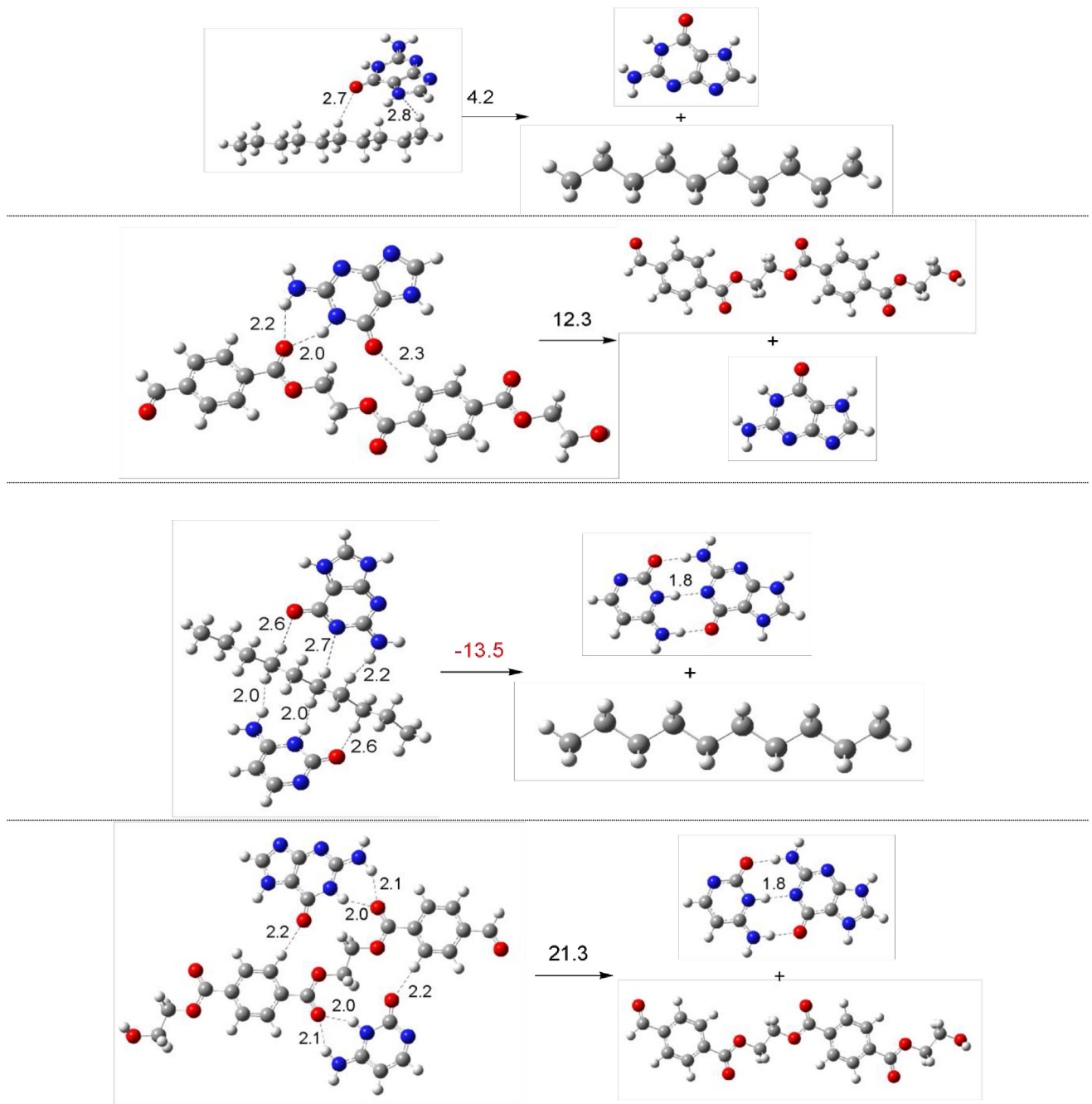
Fig 7. Optimized structures and dissociation energies (in kcal/mol) of oligomers of polyethylene ($C_{10}H_{22}$) and PET ($C_{20}H_{18}O_8$) interacting with guanine and guanine-cytosine pair. Dissociation Energies (E_{dis}, Kcal/mol) and corresponding chemical equation indicated with the optimized structures.

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Author Contributions

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Formal analysis: Ana Martínez.

Investigation: Ana Martínez, Andrés Barbosa.

Methodology: Andrés Barbosa.

Writing – original draft: Ana Martínez.

Writing – review & editing: Ana Martínez.

References

1. Thomson RC, Olsen Y, Mitchell RP, Davis A, Rowland SJ, John AWG, et al. Lost at sea: Where is all the plastic? Science. 2004; 104, 838–838.

2. Gigault J, ter Halle A, Baudrimont M, Pascal PY, Gauffre F, Phi TL, et al. Current opinion: What is a nanoplastic? Environmental Pollution. 2018; 235, 1030–1034. https://doi.org/10.1016/j.envpol.2018.01.024 PMID: 29370948

3. Kwak JI, An YJ. Microplastic digestion generates fragmented nanoplastics in soils and damages earthworm spermatogenesis and coelomocyte viability. J. Hazard. Mater. 2021; 402, 124034. https://doi.org/10.1016/j.jhazmat.2020.124034 PMID: 33254833

4. Liu P, Qian L, Wang H, Zhan X, Lu K, Gu C, et al. New insights into the aging behavior of microplastics accelerated by advanced oxidation processes. Environ. Sci. Technol., 2019; 53 (7), 3579–3588. https://doi.org/10.1021/acs.est.9b00493 PMID: 30829479

5. Mao R, Lang M, Yu X, Wu R, Yang X, Guo X. Aging mechanism of microplastics with UV irradiation and its effects on the adsorption of heavy metals. J. Hazard. Mater. 2020, 393, 122515. https://doi.org/10.1016/j.jhazmat.2020.122515 PMID: 32197203

6. Lambert S, Wagner M. Characterisation of nanoplastics during the degradation of polystyrene. Chemosphere. 2016; 145, 265–268. https://doi.org/10.1016/j.chemosphere.2015.11.078 PMID: 26688263

7. Lim XZ, Microplastics are everywhere-but are they harmful? Nature. 2021; 593, 22–25. https://doi.org/10.1038/d41586-021-01143-3 PMID: 33947993

8. Nor NHM, Kooi M, Diepens NJ, Koelmans AA. Lifetime accumulation of microplastic in children and adults. Env. Sci. Technol. 2021; 55, 5084–5096. https://doi.org/10.1021/acs.est.0c07384

9. Marcus Eriksen M, Cowger W, Erdle LM, Coffin S, Villarrubia-Gómez P, Moore ChJ, et al. A growing plastic smog, now estimated to be over 170 trillion plastic particles afloat in the world's oceans—Urgent solutions required. PLoS ONE. 2023; 18, e0281596. https://doi.org/10.1371/journal.pone.0281596 PMID: 36888681

10. Miller ME, Hamann M, Kroon FJ. Bioaccumulation and biomagnification of microplastics in marine organisms: A review and meta-analysis of current data. PLoS ONE. 2020; 15, e0240792. https://doi.org/10.1371/journal.pone.0240792 PMID: 33064755

11. Danopoulos E, Twiddy M, Rotchell JM. Microplastic contamination of drinking water: A systematic review. PLoS ONE. 2020; 15(7):e0236838. https://doi.org/10.1371/journal.pone.0236838 PMID: 32735575

12. Rotchell JM, Jenner LC, Chapman E, Bennett RT, Bolanle IO, Loubani M, et al. Detection of microplastics in human saphenous vein tissue using µFTIR: A pilot study. PLoS ONE. 2023; 18(2): e0280594. https://doi.org/10.1371/journal.pone.0280594.

13. Wang L, Wub WM, Bolan NS, Tsang DCW, Lie Y, Qina M, et al. Environmental fate, toxicity and risk management strategies of nanoplastics in the environment: Current status and future perspectives. Journal of Hazardous Materials. 2021; 401, 123415. https://doi.org/10.1016/j.jhazmat.2020.123415 PMID: 32763705

14. Shen M, Zhang Y, Zhu Y, Song B, Zeng G, Hu D, et al. Recent advances in toxicological research of nanoplastics in the environment: A review. Env. Pollution. 2019; 252, 511–521. https://doi.org/10.1016/j.envpol.2019.05.102 PMID: 31167159

15. Barria C, Brandts I, Tort L, Oliveira M, Teles M, Effect of nanoplastics on fish health and performance: A review. Mar. Pollut. Bull. 2020; 151, 110791. https://doi.org/10.1016/j.marpolbul.2019.110791 PMID: 32056587

16. Della Torre C, Bergami E, Salvati A, Faleri C, Cirino P, Dawson KA, et al. Accumulation and embryotoxicity of polystyrene nanoparticles at early stage of development of sea urchin embryos *Paracentrotus lividus*. Env. Sci. Technol. 2014; 48(20), 12302–12311. https://doi.org/10.1021/es502569w PMID: 25260196

17. Saavedra J, Stoll S, Slaveykova VI. Influence of nanoplastic surface charge on eco-corona formation, aggregation and toxicity to freshwater zooplankton. Env. Pollut., 2019, 252, 715–722. https://doi.org/10.1016/j.envpol.2019.05.135 PMID: 31185361

18. Gaylarde CC, Baptista Neto JA, da Fonseca EM. Nanoplastics in aquatic systems—are they more hazardous than microplastics? Env. Pollut. 2021; 272, 115950. https://doi.org/10.1016/j.envpol.2020.115950 PMID: 33303235

19. Teng M, Zhao X, Wang Ch, Wang Ch, White JC, Zhao W, et al. Polystyrene nanoplastics toxicity to zebrafish: dysregulation of the brain-intestine-microbiota Axis. ACS Nano. 2022; 16, 8190–8204. https://doi.org/10.1021/acsnano.2c01872 PMID: 35507640

20. Sendra M, Sparaventi E, Novoa B, Figuera A. An overview of the internalization and effects of microplastics and nanoplastics as pollutants of emerging concern in bivalves. Science Total Env. 2021; 753, 142024. https://doi.org/10.1016/j.scitotenv.2020.142024 PMID: 33207452

21. Liu X, Zhao Y, Dou J, Hou Q, Cheng J, Jiang X. Bioeffects of inhaled nanoplastics on neurons and alteration of animal behaviors through deposition in the brain. Nano Lett. 2022; 22, 1091–1099. https://doi.org/10.1021/acs.nanolett.1c04184 PMID: 35089039

22. De Felice B, Ambrosini R, Bacchetta R, Ortenzi MA, Parolini M. Dietary exposure to polyethylene terephthalate microplastics (PET-MPs) induces faster growth but not oxidative stress in the giant snail *Achatina reticulata*. Chemosphere. 2021; 270, 129430. https://doi.org/10.1016/j.chemosphere.2020.129430

23. Lehner R, Weder Ch, Petri-Fink, Rothen-Rutishauser B. emergence of nanoplastic in the environment and possible impact on human health. Environ. Sci. Technol. 2019; 53, 1748–1765. https://doi.org/10.1021/acs.est.8b05512 PMID: 30629421

24. Keinänen O, Dayts EJ, Rodríguez C, Sarrett SM, Brennan JM, Sarparanta M, et al. Harnessing PET to track micro- and nanoplastics in vivo. Scientific Reports. 2021; 11, 11463. https://doi.org/10.1038/s41598-021-90929-6 PMID: 34075133

25. Leslie HA, van Velzen MJM, Brandsma SH, Vethaak AD, Garcia-Vallejo JJ, Lamoree MH. Discovery and quantification of plastic particle pollution in human blood. Environment Int. 2022; 163, 107199. https://doi.org/10.1016/j.envint.2022.107199 PMID: 35367073

26. Sh Yang, Cheng Y, Chen Z, Liu T, Yin L, Pu Y, et al. In vitro evaluation of nanoplastics using human lung epithelial cells, microarray analysis and co-culture model. Ecotox. Envir. Safety. 2021; 226, 112837. https://doi.org/10.1016/j.ecoenv.2021.112837

27. Fragão J, Bessa F, Otero V, Barbosa A, Sobral P, Waluda CM, et al. Microplastics and other anthropogenic particles in Antarctica: Using penguins as biological samplers. Science Total Environmental 2021; 788, 147698. https://doi.org/10.1016/j.scitotenv.2021.147698 PMID: 34134362

28. Geyer R, Jambeck JR, Law KL. Production, use, and fate of all plastics ever made. Science Adv. 2017; 3 (7), e1700782. 7. https://doi.org/10.1126/sciadv.1700782 PMID: 28776036

29. Palacios-Mateo C, van der Meer Y, Seide G. Analysis of the polyester clothing value chain to identify key intervention points for sustainability. Environ. Sci. Eur. 2021; 33, 2. https://doi.org/10.1186/s12302-020-00447-x PMID: 33432280

30. Henry B, Laitala K, Klepp IG. Microfibres from apparel and home textiles: Prospects for including microplastics in environmental sustainability assessment. Sci. Total Environ. 2019; 652, 483–494. https://doi.org/10.1016/j.scitotenv.2018.10.166 PMID: 30368178

31. Majumdar A, Shukla S, Singh AA, Arora S. Circular fashion: Properties of fabrics made from mechanically recycled poly-ethylene terephthalate (PET) bottles. Resources, Conservation and Recycling. 2020; 161, 104915. https://doi.org/10.1016/j.resconrec.2020.104915

32. Rossi G, Barnoud J, Monticelli L. Polystyrene Nanoparticles Perturb Lipid Membranes J. Phys. Chem. Lett. 2014; 5, 241–246. https://doi.org/10.1021/jz402234c PMID: 26276207

33. Wang Q, Zhang Y, Rogers WJ, Mannan MS. Molecular simulation studies on chemical reactivity of methylcyclopentadiene. Journal of Hazardous Materials 2009; 165, 141–147 https://doi.org/10.1016/j.jhazmat.2008.09.087 PMID: 19013020

34. Rawat P, Singh RN. Experimental and theoretical study of 4-formyl pyrrole derived aroylhydrazones. Journal of Molecular Structure 2015; 1084, 326–339 http://dx.doi.org/10.1016/j.molstruc.2014.12.045

35. Villaverde JJ, Lõpez-Goti C, Alcamí M, Lamsabhi AM, Alonso-Pradosa JL, Sandín-España P. Quantum chemistry in environmental pesticide risk assessment. Pest. Manag. Sci. 2017; 73: 2199–2202 https://doi.org/10.1002/ps.4641 PMID: 28618212

36. Ekner-Grzyb A, Duka A, Grzyb T, Lopes I, Chmielowska-Bąk J. Plants oxidative response to nanoplastic. Front. Plant Sci. 2022, 13:1027608. https://doi.org/10.3389/fpls.2022.1027608 PMID: 36340372

37. Ferrante MC, Monnolo A, Del Piano F, Mattace Raso G, Meli R. The pressing issue of micro- and nanoplastic contamination: profiling the reproductive alterations mediated by oxidative stress. Antioxidants 2022, 11: 193. https://doi.org/10.3390/antiox11020193 PMID: 35204076

38. Ding R, Ma Y, Li T, Sun M, Sun Z, Duan J. The detrimental effects of micro-and nano-plastics on digestive system: An overview of oxidative stress-related adverse outcome Science Tot. Env. 2023, 878: 163144. https://doi.org/10.1016/j.scitotenv.2023.163144

39. Zhou Y, He G, Jiang H, Pan K, Liu W. Nanoplastics induces oxidative stress and triggers lysosome-associated immune-defensive cell death in the earthworm *Eisenia fetida*. Env. Int. 2023, 174: 107899. https://doi.org/10.1016/j.envint.2023.107899.

40. Rias U, Singh N, Banoo S. Theoretical studies of conducting polymers: a mini review. New J. Chem. 2022; 46, 4954–4973.

41. Suramitr S, Meeto W, Wolschann P, Hannongbua S. Understanding on absorption and fluorescence electronic transitions of carbazole-based conducting polymers: TD-DFT approaches. Theor. Chem. Acc. 2010; 125, 35–44. https://doi.org/10.1007/s00214-009-0655-4

42. Frisch MJ, Trucks GW, Schlegel, HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 09, Revision A.08, Wallingford, CT, 2009. D.01, Wallingford CT: Gaussian, Inc. (2013)

43. Zhao Y, Truhlar DG. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. Theor. Chem. Account. 2008; 120, 215–241. https://doi.org/10.1007/s00214-007-0310-x

44. Petersson GA, Bennett A, Tensfeldt TG, Al-Laham MA, Shirley WA, Mantzaris J. A complete basis set model chemistry. I. The total energies of closed-shell atoms and hydrides of the first-row elements. J. Chem. Phys. 1988; 89, 2193–2218. https://doi.org/10.1063/1.455064

45. Petersson GA, Al-Laham MA. A Complete Basis Set Model Chemistry. II. Open-Shell Systems and the Total Energies of the First-Row Atoms. J. Chem. Phys., 1991, 94, 6081–6090. http://dx.doi.org/10.1063/1.460447

46. Geerlings P, Chamorro E, Chattaraj PK, De Proft F, Gázquez JL, Liu S, et al. Conceptual density functional theory: status, prospects, issues. Theor. Chem. Acc. 2020; 139, 36.

47. Wang B, Rong C, Chattaraj PK, Liu S. A comparative study to predict regioselectivity, electrophilicity and nucleophilicity with Fukui function and Hirshfeld charge. Theor. Chem. Acc. 2019; 138, 12. https://doi.org/10.1007/s00214-019-2515-1

48. Gázquez JL, Cedillo A, Vela A. Electrodonating and Electroaccepting Powers. J. Phys. Chem. A. 2007; 111, 1966–1970. https://doi.org/10.1021/jp065459f PMID: 17305319

49. Gázquez JL. Perspectives on the Density Functional Theory of Chemical Reactivity. J. Mex. Chem. Soc. 2008; 52, 3–10.

50. Pearson RG. Chemical hardness: applications from molecules to Solids, Wiley-VCH, Oxford, (1997).

51. Pearson RG. Hard and Soft Acids and Bases. J. Am. Chem. Soc. 1963; 85, 3533–3539. https://doi.org/10.1021/ja00905a001

52. Pearson RG. Hard and soft acids and bases, HSAB, part 1: Fundamental principles. J. Chem. Educ. 1968; 45, 581–587. https://doi.org/10.1021/ed045p581

53. Parr RG, Pearson RG. Absolute hardness: companion parameter to absolute electronegativity. J. Am. Chem. Soc. 1983; 105, 7512–7516. https://doi.org/10.1021/ja00364a005

54. Martínez A, Rodríguez-Gironés MA, Barbosa A, Costas M. Donator Acceptor Map for Carotenoids, Melatonin and Vitamins. J. Phys. Chem. A. 2008; 112, 9037–9042. https://doi.org/10.1021/jp803218e PMID: 18714976

55. Cerón-Carrasco JP, Bastida A, Requena A, Zúñiga J, Miguel B. A Theoretical Study of the Reaction of β-Carotene with the Nitrogen Dioxide Radical in Solution. J. Phys. Chem. B. 2010; 114, 4366–4372. https://doi.org/10.1021/jp911846h

56. Alfaro RAD, Gómez-Sandoval Z, Mammino L. Evaluation of the antiradical activity of hyperjovinol-A utilizing donor-acceptor maps. J. Mol. Model. 2014; 20, 2337. https://doi.org/10.1007/s00894-014-2337-y PMID: 25069138

57. Martínez A. Donator−Acceptor Map and Work Function for Linear Polyene-Conjugated Molecules. A Density Functional Approximation Study. J. Phys. Chem. B. 2009; 113, 3212–3217. https://doi.org/10.1021/jp8106364 PMID: 19708167

58. Martínez A, Vargas R. Electron donor–acceptor properties of metal atoms interacting with pterins. New J. Chem. 2010; 34, 2988–2995. https://doi.org/10.1039/B9NJ00805E

59. Goode-Romero G, Winnberg U, Dominguez L, Ibarra IA, Vargas R, Winnberg E, et al. New information of dopaminergic agents based on quantum chemistry calculations. Scientific Reports. 2020; 10, 21581. https://doi.org/10.1038/s41598-020-78446-4 PMID: 33299000

60. Gu JD. Biodegradability of plastics: the issues, recent advances, and future perspectives. Env. Science Poll. Res. 2021; 28,1278–1282. https://doi.org/10.1007/s11356-020-11501-9 PMID: 33190206

61. Venkatesan R, Santhamoorthy M, Alagumalai K, Haldhar R, Raorane CJ, Raj V, et al. Novel approach in biodegradation of synthetic thermoplastic polymers: an overview. Polymers. 2022; 14, 4271. https://doi.org/10.3390/polym14204271 PMID: 36297849

62. Corsi I, Bellingeri A, Eliso MC, Grassi G, Liberatori G, Murano C, et al. Eco-interactions of engineered nanomaterials in the marine Environment: towards an eco-design framework. Nanomaterials 2021, 11: 1903. https://doi.org/10.3390/nano11081903 PMID: 34443734