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Comments on the Hydrolytic Degradation of Polyesters

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1. Fundamental properties of polyesters

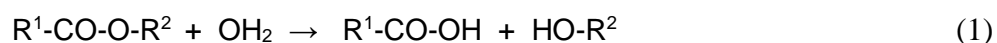
Polyesters, including polycarbonates, differ from other polymer classes in that they are sensitive to hydrolytic degradation typical for the human environment, meaning oceans, lakes, rivers and any kind of private or technical composting. Polyamides and polyurethanes may be hydrolysed upon heating with strong acids or strong bases, but such conditions do not exist on 99.9% of the surface of the Earth. The most widely used polymers, such as poly(olefins) and vinyl polymers (including polystyrene), but also polyethers, are totally insensitive to hydrolytic degradation. The hydrolytic degradation of polyesters will typically go down to the level of monomers (their building blocks), provided that enough time is available. The rate of hydrolytic degradation of polyesters may vary by a factor of 1 000 or more depending on the chemical and physical parameters discussed below in more detail.

2. Reaction mechanisms of hydrolysis

For the hydrolytic cleavage of ester groups, the following four reaction mechanisms were identified in the first half of the last century:

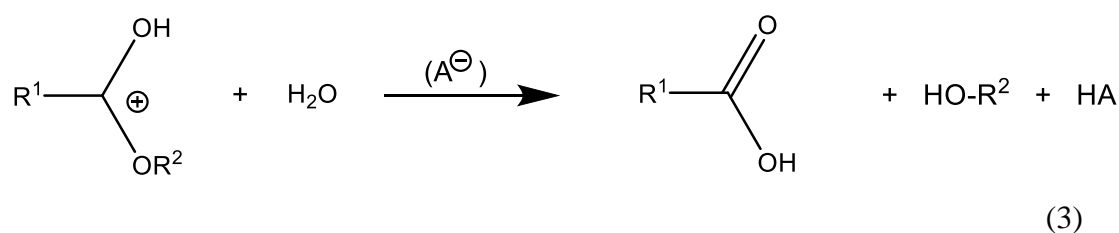
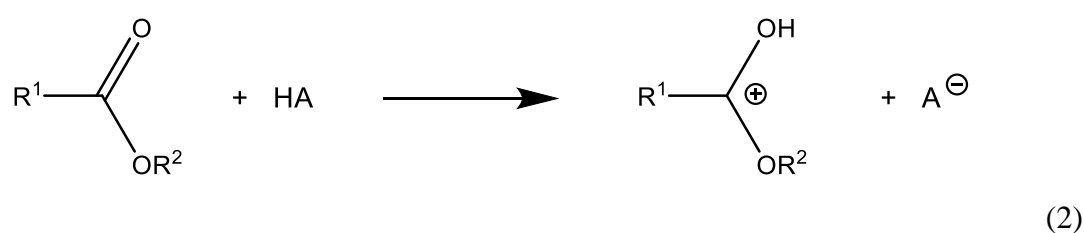
- I. Hydrolysis by neutral water
- II. Hydrolysis catalysed by acids (HA)
- III. Hydrolysis catalysed by bases
- IV. Hydrolysis catalysed by enzymes

(I) Hydrolysis by neutral water



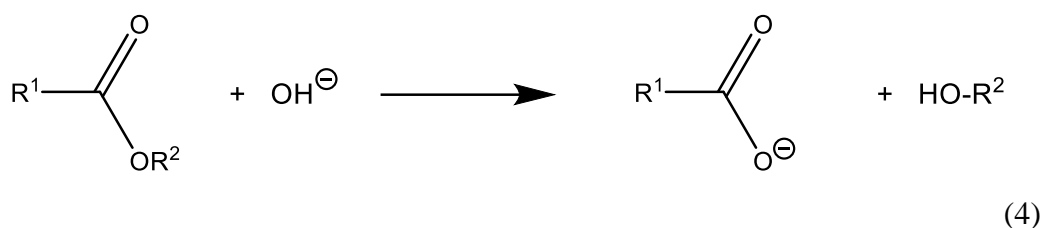
Water reacts as a nucleophile (reagent having a free pair of electrons) with the carbonyl group of the ester (the electrophile), whereupon a carboxylic acid and an alcohol are liberated. Equation (1) is a simplification of the reality. According to Pickett and Coyle (2013), two water molecules cooperate in the hydrolysis of polyesters. The liberated carboxylic acid catalyses the further hydrolysis according to mechanism (II), so that this kind of hydrolytic degradation is autocatalytic. Hydrolysis by neutral water is the slowest of all degradation mechanisms.

(II) Hydrolysis catalysed by acids (HA)



An acidic proton can protonate the carbonyl group of the ester and thus activate the electrophilicity of the ester group, so that it is more sensitive to the attack of water, with the consequence of faster hydrolysis. The rate of hydrolysis increases with acidity and concentration of the acid present in the reaction mixture. The autocatalytic effect, therefore, increases with the progress of the hydrolysis when started with neutral water. The autocatalytic effect is particularly strong for polylactide (Tsuji et al. 2002, Gorassi et al. 2017), but it is also documented for other polyesters (Xi-Lan et al. 2020).

(III) Hydrolysis catalysed by bases



Under alkaline conditions (pH > 7.0, typically > 8.0) the ester group is mainly attacked by the OH[⊖] anion, which is roughly estimated 10 000 times more nucleophilic than H₂O, so that the rate of hydrolysis is significantly accelerated even when the concentration of the OH[⊖] anions is low. Furthermore, the alkaline hydrolysis is irreversible in contrast to all other mechanisms because the resulting carboxylate anion cannot take part in the reverse reaction (i.e. esterification). When equal deviations from pH 7 are compared, i.e. pH 5 and pH 9, the alkaline hydrolysis is faster than the acid catalysed hydrolysis.

(IV) Hydrolysis catalysed by enzymes

Almost all living organisms contain esters in the form of lipids. Hence, all organisms contain enzymes (biocatalysts) that are capable of synthesising esters. These enzymes are called lipases, and typically a living organism contains several different lipases with different specificities. Lipases can hydrolyse esters when an excess of water is present. Over the past 50 years numerous individual ‘lipases’ have been identified and isolated, and part of them are commercial and produced in larger quantities. Greimel et al. (2013) have demonstrated that two commercial lipases are non-specific with regard to the polyester structure and also highly reactive. They enable hydrolytic degradation of various kinds of polyesters down to the level of monomers.

In addition to ‘lipases’, another group of enzymes has been found capable of hydrolysing polyesters, namely ‘hydrolases’. At the current state of research, hydrolases seem to be less efficient than lipases, but further research may change this picture. ‘Hydrolases’ can even hydrolyse aromatic polyesters, and a total degradation of poly(ethylene terephthalate (PET) by hydrolases has been demonstrated. Further groups of enzymes that may hydrolyse polyesters are ‘esterases’ and ‘cutinases’. This means that in nature (e.g. in lakes) microorganisms can contribute to the total hydrolysis of polyesters, and microorganisms or isolated enzymes can be used for waste water treatment or for technical composting of polyesters. Recent reviews of enzymes degrading various classes of hydrolytically degradable polymers in particular polyesters were published by Danso et al. in 2019 and by Satti and Shah in 2020. On the average the mechanisms of hydrolysis obey the following order of increasing efficiency:

neutral H₂O < acidic H₂O ~ enzymes < alkaline H₂O.

3. Factors influencing the rate of hydrolysis

The chemical and physical factors that have an influence on the rate of hydrolytic degradation will here be discussed in the following order:

- (A) Chemical structure
- (B) Reaction conditions
- (C) Physical properties of the polyesters
- (D) Bioavailability

Ad (A) The reactivity (electrophilicity) of ester groups towards hydrolysis depends on electronic and steric factors. Electronic means that electronegative substituents in α - or β -position to the ester group enhances the electrophilicity of the CO group. For example, the O-atom in α -position typical for glycolic or lactic acid has the consequence that polyglycolide and polylactide are extraordinarily sensitive to hydrolysis relative to aliphatic polyesters based on adipic or sebacic acid. On the other hand, the π -electrons of aromatic carboxylic acids are delocalised to the CO group and reduce the electrophilicity of aromatic esters significantly. Therefore, textile fibers based on poly(ethylene terephthalate) may be washed at moderate temperatures without being hydrolysed within a few weeks.

Steric factors mean that any kind of alkyl or aryl substituent near the ester group hinders the access of water (or OH anions), and thus, reduces the rate of hydrolytic degradation. This stabilizing effect of branching is valid for branching of diols and also for that of dicarboxylic acids. Hence polyesters of cyclohexane-1,4-dicarboxylic acid are less sensitive to hydrolysis than polyesters of adipic or sebacic acid. Manufacturers which are interested in hydrolytically stable coatings or sealants produce their polyesters from aromatic dicarboxylic acid or cyclohexane dicarboxylic acid in combination with branched diols. In summary, the rate of hydrolysis decreases in the following order:

polylactide > poly(hexamethylene adipate) > poly(ethylene terephthalate) > poly(neopentandiol isophthalate).

The study of Jones and McCarthy (1995) confirms this trend for polyesters. The use of branched diols for stabilisation of poly(ester-urethane)s has also recently been reviewed (Gantrade 2020).

Ad (B) There are mainly three experimental parameters that influence the rate of hydrolytic degradation: temperature, pH and the presence/absence of catalysts. Increasing temperature accelerates almost all chemical reactions including hydrolysis, so that this parameter does not need further discussion. The influence of the pH is evident from the reaction mechanisms (II) and (III) discussed above. The rate of hydrolysis increases dramatically either when the pH decreases from 7 to 1 or when it increases from 7 to 14. Interestingly, oceans contain slightly alkaline water (pH ~7.9-8.2) and thus favor hydrolytic degradation of polyesters more than lakes or rivers containing neutral or slightly acidic water.

Ad (C) A characteristic property of several polyesters such as poly(L-lactide), poly(alkylene adipate)s, or poly(ethylene-terephthalate) and poly(butylene terephthalate) is their semi-crystalline morphology. A general trend for all semi-crystalline polyesters is that the amorphous phase is considerably more sensitive to hydrolysis than the crystalline phase. This difference may amount to a factor of 10. Detailed studies of this aspect were published for polylactides (Gorassi et al. 2017), but the trends found for poly(L-lactide) are also valid for other semi-crystalline polyesters. The polyester chains in the amorphous phase are more mobile than those in the crystalline state, and the amorphous phase contains more free volume, and both parameters favor access and reaction of water.

Hydrolysis is, of course, also favored by pores and flaws in a polyester material. Another important parameter is the surface of a work part (component). It is a general rule across all polyesters that a higher surface area/volume ratio favors hydrolysis. Either the water attacks ester bonds directly on the surface or it penetrates the surface and continues hydrolysis inside the work part. At any rate, a larger surface area eases the hydrolytic degradation. Hence, microparticles of polyester will have a rather short lifetime. The surface of larger work parts or components may be coated by a hydrophobic layer or film, such as silicon oils or hydrolytically stable polymers. Such a surface is, of course, a serious hinderance for rapid hydrolysis until the protecting layer is damaged, e.g. by milling or any other kind of mechanical stress which damages the protecting layer. The influence of various hydrophobic additives on the hydrolytic stability of poly(ester-urethane)s has been reviewed by L. Xi-Lan et al. (2020).

Ad (D) According to the ECETOC, the ‘bioavailability’ of polymers needs to be distinguished as regards physical availability (as an indicator of exposure potential) and external and internal bioavailability (ECETOC, 2020). For example, poorly soluble and particulate polymers exhibit reduced physical bioavailability and may result in limited mass transfer in terms of exposure to

microorganisms. External bioavailability may be the result of the size of certain polymer molecules that are too large to cross biological barriers such as membranes. The internal bioavailability is a prerequisite for a polymer or a degradation product to become systemically available and potentially be further degraded (systemic bioavailability).

Polymers that remain bioavailable only externally may physically accumulate and, e.g., cause obstruction of the gills of fish. In the case of hydrolytically susceptible polyester polymers, biological degradation takes place generally in two stages once physical availability is given. Larger polyester chains destruct into smaller fragments (primary degradation), which are often water soluble and taken up by cells. The polymer shifts from external to internal bioavailable molecules. Enzymes are involved in the hydrolysis, and in the case of some polyesters, chemical and physical processes (e.g. temperature, UV radiation, pH, etc.) also play a role. Variability of physical/chemical environments may explain the differences of degradation kinetics of polyesters in different environmental compartments. It is also known that specificity of enzymes results in differences of hydrolytic efficiencies; hence, competent microorganisms may accelerate primary and ultimate degradation by promoting bioavailability of assessable molecules. In addition to size, the systemic bioavailability of a polymer product is dependent upon further physico-chemical properties, including charge, solubility and partitioning in water and/or biological media, and physical state. Because the degradation of polyester by hydrolysis results in the formation of the monomer or oligomers, the ecotoxic effects of the monomer/oligomer become an important factor for the evaluation of the hazard and risk potential of polyester. Due to their ester bonds, systemic bioavailable oligomeric fragments are broken down further into their monomers until they are mineralised or converted into new biomass (ultimate biodegradation).

Biodegradable polyesters

Over the past 30 years academic research and technical production of biodegradable polyesters have gathered speed stimulated by increasing environmental pollution with 'immortal' plastic.

Biodegradable polyesters are characterized by:

- 1) Hydrolytic degradation occurs in the natural environment (including the human body) within a few months (when amorphous) or within a few years (when crystalline).
- 2) The hydrolytic degradation is caused by water, and catalysts such as enzymes are not needed.

3) The degradation products are non-toxic and can be metabolised by most micro- or macroorganisms.

Excluding the kinetic data, the rules and trends found in those studies are also valid for other polyesters. The review article of Gorarasi et al. (2017) provides all details of interest.

The rates of hydrolysis of the most common biodegradable polyesters decrease in the following order:

Polyglycolide > polylactide > poly(butylene succinate) > poly(butylene adipate) > polycaprolactone.

Oligoesters

All polyesters prepared by polycondensation (i.e. all technically produced polyesters) contain oligomers which may have a linear or cyclic architecture. Linear oligomers are formed in the first stage of a polycondensation, but the fraction of cycles increases with the conversion at the expense of the linear oligomers and polymers. The cyclic oligomers contain more energetically unfavorable conformations than linear chains, which are more reactive, and thus are slightly more sensitive to hydrolysis than linear chains. Furthermore, the hydrolysis of one single ester bond suffices to transform a cyclic into a linear oligomer. The carboxylic groups liberated upon hydrolysis of the cyclics catalyse, in turn, hydrolysis of ester groups via the cationic mechanism (II). Moreover, low oligomers are easily washed out of the polymer and leave free volume that eases migration of water into the polyester. In summary, oligomers favor hydrolytic degradation of polyesters regardless of whether their topology is cyclic or linear.

List of low toxic monomers

In several countries, such as the USA, Canada and Australia, lists of monomers have been compiled that allow for reduced registration requirements for polyesters made only of monomers from this list. These lists were established before the year 2 000 and need to be updated. For example, terephthalic acid is missing as are the monomers liberated from hydrolysis of biodegradable polyesters, such as polylactide, polyglycolide, poly(ϵ -caprolactone) and poly(butylene succinate). Since lactic acid and succinic acid belong to the metabolism of most living organisms, it is *a priori* clear that dilute solutions of these monomers are not toxic.

Conclusion

Polyesters are a group of polymers which differs from all other groups of polymers in that they can be hydrolysed in any natural environment providing sufficient water. Hydrolysis may proceed just by reaction with water (more rapidly when the pH deviates from 7.0) or in the presence of enzymes (neat or via microorganisms). The rates of hydrolytic degradation may vary by a factor of 1 000 depending on structure and reaction conditions, but finally all polyesters will be hydrolysed down to their (non-toxic) building blocks. Polyesters will, due to their degradation, certainly not contribute to environmental pollution with microplastic particles surviving for hundreds of years. In this connection a recent review of Shen et al. (2020) entitled 'Hydrolysis and Solvolysis as Benign Routes for the End-of- Life Management of Thermoset Polymer Waste' should be mentioned.

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