

Review article

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Polymer degradation: a short review

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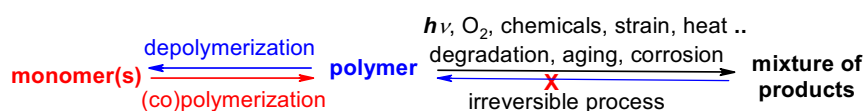
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Abstract: The reader will find basic knowledge about the degradation of polymers, its causes, course and consequences in a broader context, as indicated through the list of the chapter titles: Introduction; Depolymerization; Initiated cleavage (degradation) of macromolecules; Thermal degradation; Photochemical degradation; Mechanochemical degradation; Oxidative degradation; Polymer burning; Kinetics of cleaving macromolecules when chain depolymerization is negligible; Degradation in polymer recycling; Protection of polymers against degradation.

Keywords: depolymerization; kinetics and mechanism; polymer burning; polymer degradation; polymer recycling.

Introduction

Degradation is the act of reducing something or someone to a less respected state. In polymer science, **degradation** generally refers to a complex process by which a polymeric material exposed to the environment and workload loses its original properties (Horie et al., 2004). Degradation is usually an unwanted process. In certain cases, however, controlled polymer degradation is useful. For example, it can improve the processability of the polymer or it can be used in the recycling or natural decomposition of waste polymer (Jellinek, 1978). In the vast majority of cases, the cleavage of macromolecules is an integral part of the **polymer degradation**. Therefore, in a narrower sense, the very process of cleaving macromolecules into fragments of various structures and sizes is often referred to as polymer degradation (Jellinek, 1978). However, if monomer(s) are the final product, the cleavage is **depolymerization**, since it is the opposite of polymerization (Horie et al., 2004; Penczek et al., 2008) (Scheme 1).



Scheme 1: Relation among polymerization, depolymerization and degradation.

Degradation in which the cleavage of macromolecules is not the dominant process is commonly referred to as **polymer aging** or **corrosion** (Jellinek, 1978). Degradation induced by organisms or isolated enzymes or by a concerted action of natural environment is called **biodegradation** (Vert et al., 2020; Webb, Arnott, Crawford, & Ivanova, 2013).

Depolymerization

Like any other chemical reaction, depolymerization takes place only if it leads to a decrease in the Gibbs energy of the system. If the polymer is formed by polymerization without a side product and polymerization entropy

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$\Delta S_p < 0$, it depolymerizes only at temperatures **above ceiling temperature** $T_c \equiv \Delta H_p / \Delta S_p$ ($\Delta H_p < 0$ is polymerization enthalpy). Rarely, such as in polymerization of sulfur S_8 , $\Delta S_p > 0$ and also $\Delta H_p > 0$, and thus depolymerization prevails **below** so-called **floor temperature** $T_f \equiv \Delta H_p / \Delta S_p$ (Penczek et al., 2008). If the polymer is formed by polycondensation such as polyesterification and polyamidation, the byproduct is involved in the polymer-monomer(s) equilibrium and, if present (added), it promotes depolymerization. However, the temperature is of key importance even in these cases.

The **ideal chain depolymerization** can proceed in a living polymerization system where each macromolecule has the end-group with an active center (radical, ionic). As the activation Gibbs energy of propagation as well as depropagation is low, such system responds to the increase in temperature by the gradual release of monomer molecules from active ends of living chains, until the new equilibrium between the polymer and monomer molecules is reached. This is so-called **chain-end cleavage** mode frequently dubbed **unzipping**. Eventual subsequent temperature return results in reintegration of monomer molecules into macromolecules. The almost **ideal stepwise depolymerization** takes place in the hydrolysis of the water-soluble polyester in a dilute aqueous solution (reverse of polyesterification). In this case, each ester bond can be cleaved in the next time interval with the same probability, which is the **random cleavage** mode (Jellinek, 1978; Montroll & Simha, 1940; Vohlídal, 1994).

Initiated cleavage (degradation) of macromolecules

A polymer without active centers is currently stable at temperatures significantly above T_c , because of high activation Gibbs energy of the centers formation. It is thermodynamically unstable, but kinetically stable. However, the polymer starts to degrade when active centers are formed in it: after initiation. The dominant active centers of degradation are radicals that are created in a polymer thermally, photochemically, mechanochemically or by an oxidation process. *The type of initiation is used as adjective denoting the type of polymer degradation.*

Thermal degradation

The increase in temperature amplifies intramolecular vibrations and accelerates conformational changes of macromolecules. The intra-chain chemical bonds that are sufficiently stressed by these motions homolytically dissociate giving rise to the fragments with radical end-groups. These radicals allow depolymerization (unzipping) of the fragments at $T > T_c$ and their other reactions depending on the surroundings, typically oxidation when exposed to air.

Photochemical degradation

In a typical photochemical degradation, depending on the photon energy, radiation may electronically excite and thus make reactive some groups in the polymer (light, UV), or dissociate some its bonds to radicals (UV, RTG), or eject an electron from the molecule (RTG, γ -rays) giving rise to radical-ions (Guillet, 1980, 1985, Ranby & Rabek, 1975). Depending on the polymer structure and ambient conditions, the photogenerated species depolymerize (at $T > T_c$) and/or enter various subsequent reactions resulting in the cleavage or crosslinking or modification of polymer molecules or all. When it occurs in air, photochemical initiation is followed by oxidation of the polymer (see below) and the overall complex process is called **photooxidative degradation** (Jellinek, 1978). Thermal and chemical degradations promoted by microwave or infrared radiation are not considered photochemical, but as the radiation-assisted degradations.

Mechanochemical degradation

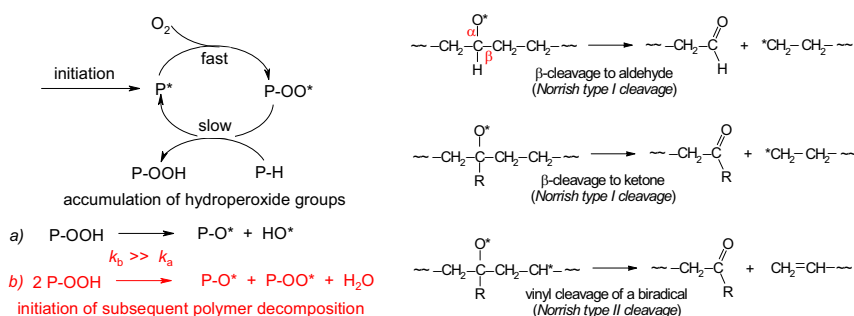
When one breaks a rubber band, he actually breaks a lot of chemical bonds of the original network macromolecule. A linear macromolecule can be also mechanically broken to two radical fragments if sufficient mechanical work is supplied to it via intermolecular interactions under flow shear stress (Ballauff and Wolf, 1984; Netopilík et al., 1990). Such cleavage is unseen for small molecules onto which the energy required to rupture cannot be transferred in this way. Efficient energy transfer by shear in flow is only possible on long molecules (Jellinek, 1978). Accordingly, the **mid-chain cleavage** mode is typical of this degradation. Shear degradation is desired for example in preparation of rubber mixtures by calendaring (before vulcanization). Some rubbers namely contain large portions of macromolecules with the relative molecular weight (MW) more than one million, whose cleavage significantly reduces the viscosity of the vulcanization mixture, thus achieving faster and better homogenization of the mixture. On the other hand, the flow-induced degradation is undesirable though present in the SEC (Size Exclusion Chromatography) columns where the cleavage of long linear macromolecules, typically those with MW over two millions, distorts the measured MW distribution of a polymer (Barth & Carlin, 1984; Striegel, 2008). The mid-chain cleavage can be also induced by the ultrasound which imposes periodic conformational changes on macromolecules that cause them to rupture (Peterson et al., 2020).

Oxidative degradation

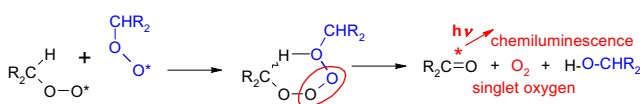
Oxidative degradation is the branched radical chain reaction that always participates in corrosion of polymers exposed to air. It can be **initiated intentionally** by processes indicated above, or it can occur spontaneously - then it is called **autoxidation**. The latter is typical of conjugated polymers that contain delocalized free radicals (Bondarev, Zednik, Plutnarova, Vohlídal, & Sedláček, 2010; Vohlídal, Rédrová, Pacovská, & Sedláček, 1993). Although these radicals are stabilized by delocalization to such an extent that they do not react with molecules, they easily react with the atmospheric oxygen, each molecule of which contains two unpaired electrons in the ground state. Because this ground state is the triplet state, the current “low-reactive” form of oxygen is called **triplet oxygen** (Guillet, 1985).

A typical oxidative degradation shows a long lasting induction period in which the hydroperoxyl side groups are gradually formed and accumulated in the polymer. The $-OOH$ groups only negligibly contribute to oxidation in this reaction stage, since the first-order rate constant of a hydroperoxide dissociation at 30 °C is of the order of 10^{-8} s^{-1} . However, if concentration of $-OOH$ groups is increased enough, their more energy-efficient bimolecular decomposition begins. This strongly accelerates the overall degradation rate and, as a result, the polymer rapidly loses its original properties. Therefore, one can usually see almost no change in the polymer quality for a few or many years and then a rapid decrease in the quality within a few weeks or months. In contrast, conjugated polymers of monosubstituted acetylenes degrade without a visible induction period when exposed to air though they are long-time stable in vacuum or under inert atmosphere (Kabátek, Gas, & Vohlídal, 1997; Vohlídal, Kabátek, Pacovská, Sedláček, & Grubisic-Gallot, 1996).

In oxidative degradation, macromolecules are mostly cleaved by the β -fission processes (see Scheme 2) to fragments with aldehyde, ketone and vinyl end-groups (Dan & Guillet, 1973; Norrish & Bamford, 1937, 1938). Other groups abundant in the degradation products are $-OH$ groups formed by radical-transfer reactions such as $P-O^* + P-H \rightarrow P-OH + P^*$. The molar absorption coefficients of the IR bands characteristic of carbonyl groups (at around 1700 cm^{-1}) are mostly very high. Therefore, the IR spectra are widely used for monitoring the oxidative polymer degradations. Another phenomenon accompanying these degradations is **chemiluminescence**. The fact that its intensity is proportional to the square of the concentration of peroxy radicals indicates that it originates from disproportionation of $P-OO^*$ radicals (Scheme 3). The energy released in this reaction ($>400 \text{ kJ/mol}$) fairly exceeds the energy needed to electronically excite keto groups (ca 300 kJ/mol). The excited keto groups then emit radiation during their transitions to the ground state. Moreover, a significant



Scheme 2: Main reactions participating in the polymer oxidative degradation.



Scheme 3: Disproportionation of hydroperoxyl radicals – source of singlet oxygen and luminescence.

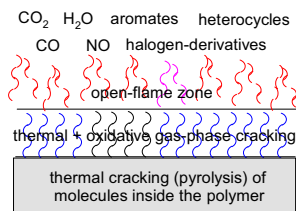
portion of the oxygen formed in the disproportionation of -OOH groups is in the electronically excited singlet state that is extremely reactive. It is so-called **singlet oxygen** which immediately enters reactions giving new peroxides and peroxy radicals, so accelerating the overall polymer degradation (Jellinek, 1978).

Oxidative polymer degradation is generally monitored by various spectroscopic methods differing in the type of information provided and in the detection limit. The kinetics of this process is often studied by the “oxygen uptake” method. The surface polymer degradation can be effectively studied by using Raman, infrared or special electronic spectroscopy. However, it should be stressed that all those methods provide only indirect evidences of shortening of the polymer molecules. Such information is mostly obtained by the size exclusion chromatography (SEC) method which is very effective (sensitive) in detecting the early stage of degradation. Consider for example that the number-average degree of polymerization $\langle X \rangle_n$ of a polymer drops from 2000 to 1000 exclusively by β -scission processes whose each gives two fragments: one with and one without carbonyl end-group. There is no doubt that SEC will reliably detect this drop in $\langle X \rangle_n$. However, the mole fraction of monomeric units with carbonyl group in the final polymer (0.0005) will mostly be significantly below the detection limit of spectroscopic methods. The SEC method also provides information how the molar-mass distribution of the polymer changes during the degradation, which helps to understand the overall process (Bondarev, Trhlíková, Sedláček, & Vohlídal, 2014; Trhlíková, Hladyš, Sedláček, & Bondarev, 2016).

Polymer burning

Polymer burning is the extreme (limiting) case of the polymer oxidative degradation. One might think that polyethylene, as a high molecular weight alkane, will burn similarly to gasoline or diesel, whose vapors form homogeneous mixtures with air, in which they can burn out almost perfectly. However, the gaseous state is unattainable for polymers since their boiling temperature fairly exceeds the temperature at which they decompose. Therefore, the burning of the polymer is preceded by its thermal degradation in the absence of oxygen (pyrolysis, thermal cracking) inside the polymer. This gives gasifiable fragments of polymer molecules that penetrate into zones above the polymer surface, where they mix with oxygen and burn. It is surface burning, in which the pyrolysis products are burned, not alkanes! And the products are unsaturated and aromatic hydrocarbons, heterocycles and their derivatives, mostly carcinogenic compounds. Because these compounds can partly escape from the flame zone and pollute the environment, the safe polymer combustion must be fast, which requires furnaces with operating temperatures of at least 1200–1400 °C or higher (Scheme 4).

The **fire risk** of a polymeric material is assessed by the so-called **limiting oxygen index** (LOI), which indicates the minimum molar fraction of oxygen in its mixture with nitrogen required for the material to burn



Scheme 4: Scheme of the polymer burning.

continuously without an external flame or heat source. It is measured by means of passing the oxygen + nitrogen mixture of the gradually decreasing oxygen content over a burning specimen until a flame is quenched (For LOI values see e.g. <https://omnexus.specialchem.com/polymer-properties/properties/fire-resistance-loi#values>). However, the fire risk of a polymeric material is given not only by its flammability in contact with the open flame and the flame stability (LOI), but also by the possibility of its self-ignition in an atmosphere sufficiently rich in oxygen. The auto-ignition of the polymer depends not only on its temperature, but pronouncedly also on the surrounding atmosphere pressure, because the oxygen concentration at the polymer surface is proportional to this pressure. It might be useful to know that also poly(tetrafluoroethylene) burns in a pure oxygen atmosphere (LOI = 95) and even explosively at room temperature when the oxygen pressure is high, such as for example the current pressure in oxygen steel-bottle containers (150 at).

Kinetics of cleaving macromolecules when chain depolymerization is negligible

Such cleavage is common in degradations occurring well below the ceiling temperature, for example in hydrolytic, mechano-chemical or autoxidative degradations at room temperature, i.e., at conditions under which polymers are mostly applied. The cleavage is mostly monitored by SEC and the obtained data mostly in terms of **scission index**, B , defined as the average number of cleavable bonds (typically links between monomeric units), b , that were cleaved per one initial macromolecule (Jellinek, 1978):

$$B = (b_0 - b)/N_0 \text{ from experimental data: } B = (\langle X \rangle_{n,0} / \langle X \rangle_n) - 1 \quad (1)$$

N_0 is the initial number of macromolecules in the system and b_0 initial number of links.

For **random cleavage**, in which all links have the same probability of being cleaved in a given time interval, the cleavage is formally the first-order reaction (links decay exponentially with the rate constant v : $b = b_0 e^{-vt}$ and thus $B = (b_0/N_0) \cdot (1 - e^{-vt}) = B_\infty \cdot (1 - e^{-vt})$). The rate constant v is thus obtained as the slope of the plot:

$$\ln(B_\infty - B)/B_\infty = -vt \quad (2)$$

where $B_\infty = \langle X \rangle_{n,0} - 1$. Note that a linear chain of the degree of polymerization of X contains $(X - 1)$ bonds, and that their number is the maximum number of bonds that can be cleaved per one original macromolecule. If Eq. (2) well fits the experimental data, the random scission mode can be considered but it still should be verified using additional plots, because the extent of degradation covered with experimental data is mostly not high enough and, moreover, experimental values of $\langle X \rangle_n$ (or $\langle M \rangle_n$) suffer from low accuracy. Experimental values of the weight-average degree of polymerization $\langle X \rangle_w$ or weight-average molar mass $\langle M \rangle_w$ (Stepto et al., 2015) are in general significantly more reliable. If Eq. (2) does not fit the data, another scission mode must be considered (Vohlídal, 1994). For the mechano-chemical degradation induced by the ultrasound or a hydrodynamic force field, Eq. (2) was found to be applicable, too, though it obeys the mid-chain scission mode. However, in that case, macromolecules of molar masses up to ca 100,000 g/mol are usually not cleaved and so B_∞ must be determined experimentally (Netopilik et al., 1990; Peterson et al., 2020).

Degradation in polymer recycling

The preferable way of polymer recycling is a use of the purified and suitably pretreated polymer in production of new products. This is easy in cases where the degradation of the waste polymer is so small that it is not important for the properties of the new product. For example PET bottles are chopped into pieces that are washed and used to make PET fibers for car mats and fabrics and wadding for the upholstery of armchairs and seats. The recycled high-density polyethylene (HDPE) is currently used in production of garden furniture, buckets and similar products. Nevertheless, similar procedures are not too frequently seen.

Depolymerization of the waste polymer into monomer(s) that are then used in the synthesis of new polymers is another possibility of recycling, which might be nice mainly for polymers prepared by polycondensation, such as polyesters, polycarbonates and polyamides that are depolymerized by hydrolysis or solvolysis (Webb et al, 2013). These processes require high temperatures or the microwave assistance and efficient separation and purification of obtained products. This makes them expensive; nevertheless, they are increasingly used.

Biodegradation

Polyesters prepared from natural monomers, such as well-known poly(lactic acid)s or poly(lactide)s undergo hydrolytic degradation and biodegradation to harmless natural products, which, however, lasts for up to decades in a normal natural environment. Therefore, they are so far mostly not recycled but as a waste composted and their chemical depolymerization to useful products is of steadily increasing interest (Román-Ramírez et al., 2020; Vert et al., 2020).

There are many “desirable” biodegradations of natural and specialty polymers that are widely used in the food industry and practical medicine. An example from the food industry is the enzymatic cleavage of amylose (a linear polymeric component of cereal starch) to the maltose disaccharide in the production of malt, from which beers are then produced. The best-known examples from medicine are absorbable surgical sutures and threads used in surgery. These are made from biodegradable polyesters such as random and block copolymers of glycolic acid and its cyclodimer glycolide, lactic acid or its cyclodimer lactide, ϵ -caprolactone and 1,3-dioxan-2-one (“trimethylene carbonate”). The rates of decrease in the strength of sutures and their total degradation in the body are tuned by the composition of the material (Middleton & Tipton, 2000).

Thermal degradation, i.e., pyrolytic decomposition of waste polymers into diesel, kerosene and gasoline fuels and synthetic gas is another industrially utilized way of the polymer waste treatment, though it is not the polymer recycling. These processes consume hydrogen that is needed for hydrogenation of unsaturated intermediates formed in thermal cleavage of polymer chains (Qureshi et al., 2020; Ramin, Assadi, Hussein, & Sahajwalla, 2014; Ratnasari, Nahil, & Williams, 2017).

Protection of polymers against degradation

Polymer degradation is a complex process by which the polymer loses its original functional properties owing to irreversible changes in its structure. All types of polymer reactions take part in corrosion: (i) chemical transformation of functional groups, (ii) cleavage of polymer molecules by oxidation, hydrolysis, photochemical and other chemical reactions, mechano-chemical processes and by depolymerization, and (iii) crosslinking of polymer molecules as well as their fragments. Crosslinking makes the aged polymer brittle while cleavage processes makes it waxy or sticky and, in addition, yellowish or brownish owing to unsaturated chromophores formed (Jellinek, 1978; Ranby & Rabek, 1975).

Undesirable degradation processes are significantly reduced by stabilizers admixed into the polymeric material. A single stabilizer is usually not enough; a mixture of a few stabilizers mostly has to be used.

According to the function, stabilizers are roughly divided to photostabilizers, antioxidants, antiozonants, radical scavengers, peroxide scavengers, acid scavengers, fire retardants and biocides. Because the stabilizer is in general only admixed into a polymer, not bound to it, its second key property is a good compatibility with the polymer. When the compatibility mediated by the intermolecular interactions is poor, the stabilizer is spontaneously displaced to the polymer surface by the ever-present thermal motion, from where it is removed by external influences. As a result, the polymer becomes unprotected. If a good compatible stabilizer is not accessible, a new one can be obtained by connecting one or more oligomeric chains good compatible with the polymer to an available stabilizer with the given basic function.

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