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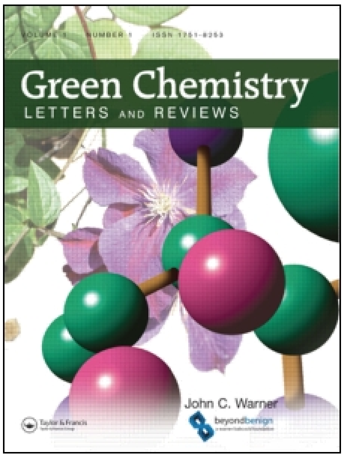

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Photodegradable plastics: end-of-life design principles

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RESEARCH REVIEW

Photodegradable plastics: end-of-life design principles

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Photochemically degradable polymers and plastics are reviewed with an emphasis on the environmental and molecular factors that control the onset of degradation and the rate of degradation. A number of principles are beginning to emerge for the design of viable photochemically degradable plastics. Among the principles discussed are those relating to the effects of chromophores, initiators, antioxidants, temperature, oxygen diffusion into the plastic, polymer crystallinity, tensile and compressive stress, and the absorbed light intensity on the plastic. To obtain a plastic with a controlled lifetime and a specific rate of degradation, many of these parameters can be controlled or adjusted in the design stage of the plastic.

Keywords: degradable plastics; end-of-life; photodegradation; autoxidation

Introduction

A key principle of green chemistry is to "design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment" (*1*). In an obvious deviation from this principle, most plastics are loaded with additives that prevent their degradation (*2*), and this has led to one of society's major sustainability problems, namely the persistence of plastics in the environment (*3*). To reduce the build-up of plastics in the environment, two general strategies have been adopted. One strategy is to recycle plastics and the other is to re-design them so they do in fact degrade into environmentally benign products (*4*). With regard to recycling, there is a growing literature on designing plastic objects so they are more easily recyclable (*5*). For example, the Association of Postconsumer Plastic Recyclers has issued guidelines and practical tips that are intended to help in designing plastic products that can be more easily recycled (*6*). Likewise, considerable work has gone into developing design principles for degradable plastics, and manufacturers have made progress in the production of such materials (*7*). Despite this progress, the chemical principles needed to develop practical degradable plastics are in need of further development. The reason further work is needed is that there is a complex synergism between the various parameters that affect the onset of degradation and the rate of plastic degradation. For example, it is known that tensile stress and temperature can impact degradation rates, but the response of plastics to the combined effects of tensile stress and temperature is unknown. Consequently, the practical application of design principles to high-performance, commercially viable plastics is still a challenge. One of the purposes of this review is to describe what is known about polymer degradation, which may help to suggest new principles of importance to the design of degradable plastics. A second purpose is simply to categorize the environmental and molecular parameters that impact the degradation of plastics. Systematic knowledge plays a crucial role in design and interpretation, and this review should serve as a starting point for the interpretation of new data.

The field of degradable plastics is an enormous area, so the primary focus of this review is limited to a smaller subset of the field, namely photochemically degradable plastics. We start with a brief overview of some descriptive aspects of photochemically degradable plastics, then we turn to a review of photochemical degradation mechanisms in polymers, and we conclude with a review of how various environmental and molecular parameters impact the photodegradation process. There is commentary throughout concerning fundamental principles of design as applied to photodegradable plastics. One final introductory comment is to note that the discussion is limited to degradable plastics that are useful for sustainability (end-of-life) purposes; degradable plastics that are used primarily for other purposes (e.g. photolithography) are not discussed.

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Design goals

The ideal properties of a photodegradable plastic are illustrated in Figure 1 (*7,8*). The key features of this figure are as follows:

- The onset of degradation should be reliably predictable. Although, it is obvious why this property is desirable for practical applications, it is noted that it is difficult to predict polymer lifetimes in practice because environmental parameters vary. For example, light intensities vary, as do temperatures and a host of other variables that control degradation rates and degradation onsets.
- The onset of degradation should be tunable. Photodegradable plastics have different applications, and each application will generally require a different lifetime. Methods must be found for manipulating polymer lifetimes.
- The plastic should degrade completely and quickly once degradation starts. This characteristic is important for practical reasons because most polymer mechanical properties are related to molecular weight. Small amounts of degradation can drastically decrease the molecular weight (and thus the mechanical properties) of a polymer, yet to all appearances the plastic piece is visually unchanged. In essence, the plastic is still present but it is not structurally sound, and hence useless and perhaps dangerous. Under such circumstances, it may as well be completely degraded.

Note that these ideal properties lead to a decay curve (Figure 1) that has a step-function shape, which, to say the least, is not a conventional shape for kinetics plots. However, several mechanisms display shapes approaching a step-function, including autocatalytic processes, cooperative mechanisms, and initiation/inhibition antagonism mechanisms. In practice, most polymers do not decay naturally by one of these mechanisms so there is room for creative synthetic innovation.

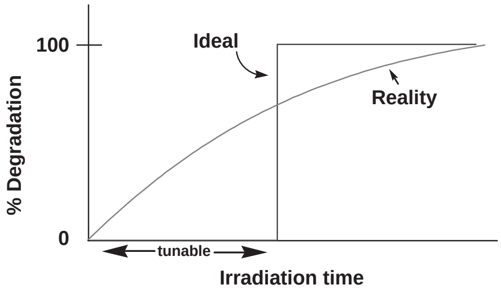


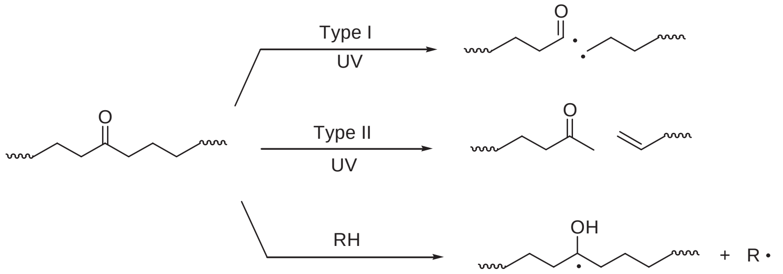
Figure 1. The degradation kinetics behavior of a typical polymer (red) and an ideal photochemically degradable polymer (blue). Note the tunable onset of degradation and the rapid degradation in the ideal polymer.

Current applications for photodegradable polymers

Photodegradable plastics have a number of practical and commercial uses for sustainability purposes. One of the major uses for these materials (and for degradable plastics, in general) is in agriculture, where they are used in a farming technique called "plasticulture" (*3*). In this application, the ground is covered with plastic sheeting (typically a polyolefin); the sheeting acts as a mulch to prevent the growth of weeds (thus requiring the use of fewer herbicides), decreases water demand, and extends the growing season by keeping the ground warmer. By making these agricultural films out of degradable plastics, considerable labor and money can be saved in the plastics recovery phase of the technique. Another growing application for photodegradable polymers is as "green" plastics, where their degradability is exploited to rid the environment of the plastic item. For example, photodegradable plastics are finding increased use as packaging material for items that have a high probability of becoming litter. Photodegradable consumer plastics have also found their way into homes as degradable trash bags and plastic kitchenware. Finally, it is noted that photodegradable polymers are also used extensively in several applications that are not related to sustainability, for example, in photolithography and in biomedical applications (*9,10*).

Photodegradable polymers: reactivity overview and design principles

Before discussing methods for making plastics photochemically degradable, it is important to note that the photochemical reactions that occur in a plastic are usually not intended to completely degrade the polymer chains to low molecular weight species. Rather, the purpose of the photochemical reactivity is to fragment the polymer chains to lower molecular weight chains and to introduce carboxylic acid, ketone, aldehyde, or alcohol end-groups onto those fragments (*4,11*). Only after this reactivity has occurred can biodegradation occur, which results in the conversion of the polymer molecules into CO_2, H_2O, and biomass. Formation of the lower molecular weight chains in the photochemical reaction is important because the plastic must be "wettable" in order to support the microorganisms that carry out the biodegradation processes. (Studies suggest a polyolefin must have a molecular weight less than $\approx$40,000 g/mol to be wettable (*11*).) The formation of the oxygenated end-groups is important for the cellular β-oxidation process that is responsible for the stepwise dismantling of the polymer chain (*12,13*).

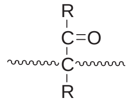


Scheme 1. The photochemical reactions of a ketone-containing polymer. Note that all of these pathways lead to polymer backbone cleavage.

Note that the two-step process consisting of the abiotic reaction (to form lower molecular weight chain fragments with oxygenated end-groups) followed by biodegradation is called "oxo-biodegradation." When the abiotic process is facilitated or speeded up by photochemical reactivity then the process is a "photochemical oxo-biodegradation." However, this latter term is usually just shortened colloquially to "photo-oxidative degradation" or "photodegradation," both of which can be misleading because they ignore the essential biodegradation reactivity component of the overall process.

Photodegradable polymers are typically designed in one of two ways: (1) by incorporating a photosensitive degradable chromophore into the backbone of the polymer chain; or (2) by mixing an additive into the polymer that initiates or facilitates degradation reactions (typically radical autoxidation reactions) within the polymer (*8,14*). The first strategy is commercially accomplished by incorporation of a carbonyl group into the backbone of polyolefins (*15*). One of the first commercially successful plastics of this type is E-CO plastic, which is manufactured by the copolymerization of ethylene and carbon monoxide in the presence of a catalyst to produce a polyketone (*4*). This polymer has been used since the 1970s to make the Hi-Cone™ six-pack rings and is still used today. The photochemistry of these types of polymers was first studied by Guillet and Hartley and their findings made the advancement of these materials a commercial possibility (*16,17*). The photodegradation of polymers containing carbonyl groups occurs by the Norrish Types I and II photochemical reactions and by hydrogen atom abstraction reactions, as illustrated in Scheme 1. Note that these photoreactions require UV radiation. Also note that the Norrish Type II reaction is a significant contributor to the degradation of polyesters and polyacrylates owing to the presence of the carbonyl group (*17,18*). Although the Norrish Types I and II reactions lead to cleavage of the polymer backbone and thus some embrittlement of the plastic, several authors have noted that the ketone-containing chains and the vinyl-terminated chains are not inherently biodegradable (*7*). The subsequent biodegradation and disappearance of the fragmented polymer is thus slow. Furthermore, the vinyl group can participate in subsequent polymerization reactions, which can increase the molecular weight of the polymer chains.

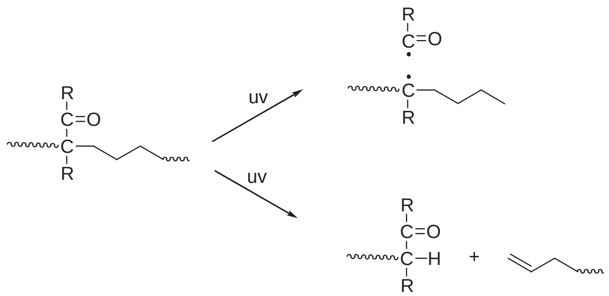
An alternative strategy is to incorporate the carbonyl group on a side-chain, as in the commercial Ecolyte polymers (*14,19*). These polymers are made by copolymerizing vinyl ketones with vinyl monomers such as ethylene or styrene to give polymers with the following structure interspersed along the backbone (*19*):



$$\sim\sim\underset{\underset{R}{|}}{\overset{\overset{\overset{R}{|}}{C=O}}{\overset{|}{C}}}\sim\sim$$

Backbone degradation occurs by the Norrish Type II route in these polymers (Scheme 2). Note that Norrish Type I photochemistry leads to the formation of radicals in these systems (Scheme 2). Once radicals are formed then autoxidation can occur, which also leads to polymer degradation. The autoxidation process is described in more detail in the following section on additives that induce photodegradation processes.

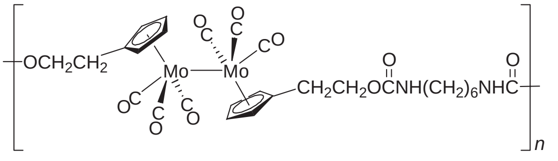
Chromophores other than C = O have been incorporated into polymer backbones to make the polymers photodegradable. These polymers are not necessarily intended for commercial application but



Scheme 2. Photochemical degradation of a polymer backbone with pendant carbonyl groups.

rather for research purposes and to elucidate the principles of polymer degradation. An example is the class of polymers with metal–metal bonds along the polymer backbones (*20*). Photochemical degradation occurs with these polymers because metal–metal bonds cleave homolytically when irradiated with visible light (Scheme 3) (*21*). Note that the metal radicals formed by photolysis can be captured with an appropriate radical trap, typically an organic halide or molecular oxygen (*21,22*).

Specific examples of such polymers are the following (*23,24*):



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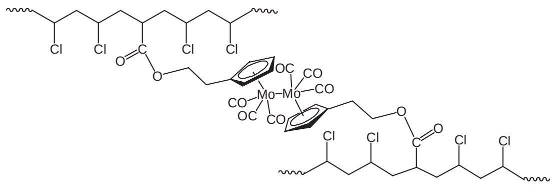

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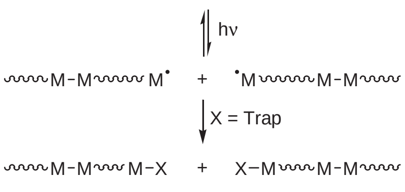
As an example of the utility of these polymers, by using polymer **2** it was possible to extract information about the effects of tensile stress on degradation rates without the mechanistic complications inherent in the degradation mechanisms of organic radicals. (For example, metal radicals do not lead to crosslinking, so this complicating feature found with organic radicals was avoided.) In the sections that follow, many of the key results that concern the effect of various parameters on degradation rates and degradation onsets were obtained with polymers that contain M–M bonds along their backbones.

The second strategy for making photodegradable polymers is to add light-activated radical initiators to the polymer. An example of such an additive is TiO_2 Equation (1). The radicals produced by these photoreactions react with oxygen to form hydroperoxide species (ROOH) in an autoxidation cycle (Scheme 4). Subsequent to hydroperoxide formation, polymer backbone cleavage generally occurs by one of two pathways: (1) cleavage of the hydroperoxide O–O bond occurs, followed by β-scission in the alkoxy radical (Scheme 5); or (2) the hydroperoxide species react to form new functional groups (typically carbonyls, alcohols, carboxylic acids, and olefins) and other chromophores. The most important of these reactions are compiled in Scheme 5, but not all of these reactions occur in every system. Polymer backbone cleavage then occurs by subsequent irradiation or thermal reactions of these functional groups and chromophores. For example, carbonyl formation leads to backbone cleavage by the Norrish Types I and II photochemical reactions (Scheme 1). It is generally agreed that the β-scission route is the prevailing pathway for backbone degradation in the photo-oxidative degradation of most polymers (*25*),

$$\mathrm{TiO_2} \xrightarrow{h\nu} \mathrm{TiO_2}^{*} \xrightarrow{O_2,\ \mathrm{RH}} \mathrm{TiO_2} + \mathrm{HOO}^{\bullet} + \mathrm{R}^{\bullet}. \qquad (1)$$



Scheme 3. Photochemical degradation of a polymer with metal–metal bonds along its backbone.

While on the topic of additives, it is interesting to note that thermally degradable plastics can also be made by the addition of additives that cause hydroperoxide formation (via formation of radicals as in Scheme 4) or by the addition of additives that facilitate the decomposition of hydroperoxides to radicals (step a in Scheme 5). Some common additives used in these thermally degradable plastics include peroxides, metal chlorides (e.g. cobalt(II), lithium, iron(III), nickel(II), copper(II), $M(acac)_n$ complexes, $M(stearate)_n$ complexes, benzophenone, and quinones (*4,8,26–29*)).

One strategy that is used to control the onset of degradation in a plastic is to add both an antioxidant and an initiator to the plastic. As long as both additives are present, degradation will be minimized. But, if slightly more initiator is present then eventually, when the antioxidant has all been consumed, oxidative degradation will start. The lifetime of the

Initiation

Initiator $\longrightarrow R_i^\bullet$

$R_i^\bullet + O_2 \longrightarrow R_iOO^\bullet$

$R_iOO^\bullet + R\text{–}H \longrightarrow R_iOOH + R^\bullet$

Propogation

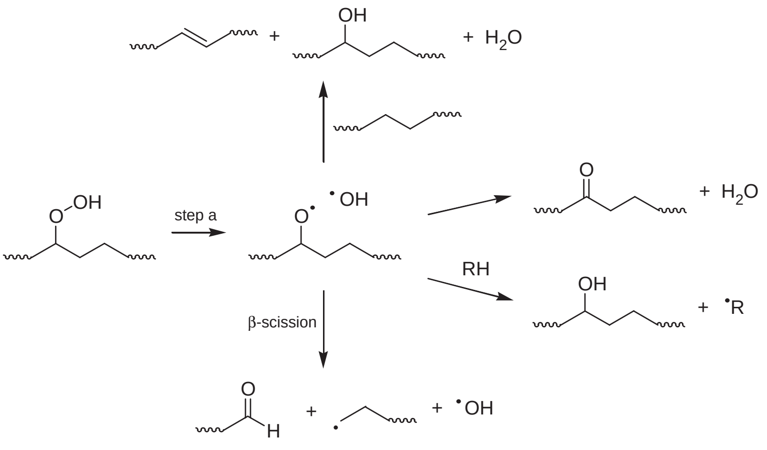
$R^\bullet + O_2 \longrightarrow ROO^\bullet$

$ROO^\bullet + R\text{–}H \longrightarrow ROOH + R^\bullet$

Termination

Radical coupling or disproportionation reactions

Scheme 4. The autoxidation process.



Scheme 5. Examples of organic hydroperoxide reactions. Note that a carbonyl chromophore can form from reaction of the hydroperoxide. The carbonyl group is a chromophore and its formation leads to subsequent photochemical reactions.

plastic can be controlled by adjusting the relative amounts of the antioxidant and the initiator. An example of this approach is used by EPI, Inc. and their additive TDPA, which is used to facilitate degradation of polyolefins. (The chemical identities of the TDPA additives are proprietary, but they are said to contain transition metal complexes with carboxylate ligands. Transition metal carboxylates facilitate degradation by catalyzing the autoxidation process. More specifically, the transition metal complexes catalyze the breakdown of the hydroperoxide species (ROOH) formed by autoxidation, as shown in Scheme 6. The catalysis mechanism, which involves redox reactions, takes advantage of the ability of transition metal complexes to convert between two oxidation states.) A variation of this principle is to use the same chemical additive as both the antioxidant and as the precursor for the initiator. The so-called Scott–Gilead system is one example where this strategy has been successfully commercialized. In this system, metal dithiocarbamates are used as the antioxidants. In this capacity, they prevent degradation of the plastic. (Metal dithiocarbamates react with hydroperoxides to prevent oxidation of the polymer chains.) However, when irradiated by UV light or when heated, the metal dithiocarbamates react to form metal carboxylate complexes, which are potent facilitators for photo-oxidation of the polymer chains. The photodegradable mulching films used in plasticulture use this technology and also the TDPA technology.

$$\mathrm{M}^{n+} + \mathrm{ROOH} \longrightarrow \mathrm{M}^{n+1} + \mathrm{RO}^{\bullet} + \mathrm{OH}^{-}$$

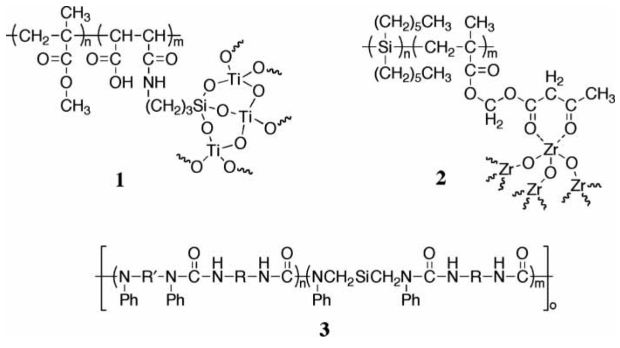
$$\mathrm{M}^{n+1} + \mathrm{ROOH} \longrightarrow \mathrm{M}^{n+} + \mathrm{ROO}^{\bullet} + \mathrm{H}^{+}$$

$$\text{Net:}\quad 2\,\mathrm{ROOH} \longrightarrow \mathrm{RO}^{\bullet} + \mathrm{ROO}^{\bullet} + \mathrm{H}^{+} + \mathrm{OH}^{-}$$

Scheme 6. Metal catalyzed degradation of hydroperoxides. Note that the RO and ROO radicals formed in the top set of reactions react further to eventually give alcohols, carboxylic acids, aldehydes, and ketones.

In a related strategy involving both an initiator and an "inhibitor" to control degradation rates, Scott (*7*) notes that the degradation of photodegradable polymers containing carbonyl chromophores is sometimes too fast in tropical climates where the sun is intense. To moderate the rate of degradation, UV absorbers are added to the plastic. The UV absorbers lower the intensity of light available to the carbonyl groups, and the rate of degradation is slowed.

Other examples of the two strategies discussed above for making photodegradable polymers are noteworthy for both their relevance to the field of polymers containing inorganic and organometallic molecules and for their innovative attributes. For example, a novel synthetic strategy is currently being explored to covalently link commonly used inorganic photosensitizers to polymer pendent groups using sol–gel synthesis techniques (Figure 2, polymers **1** and **2**) (*30,31*). Polymers containing pendant radical initiators have the advantage of discouraging large inorganic



1 **2** **3**

Figure 2. Examples of inorganic photosensitizers attached to polymer chains through pendant groups.

aggregates in the solid-state. Polysilanes (Figure 2, polymers **2** and **3**) are a class of photodegradable polymers that were primarily developed for photolithography applications, given their transparent nature and photoconductivity (*31,32*). Recent progress in this area has been made toward elucidating the mechanism of photodegradation. It was shown for the case of polyurea-containing silane units that the photodegradation pathway involves a single-electron transfer between the silyl and carbonyl groups, silyl group migration, and solvolysis (*32*).

Factors effecting degradation rates

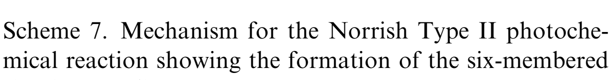
Controlling the degradation of a plastic material in a prescribed fashion so that the rate and onset of degradation are both tunable and predictable for a particular application is a complex problem. In order to achieve this goal, it is necessary to identify the experimental parameters that affect degradation rates and to determine how those parameters affect the degradation mechanism. In addition, because many of the parameters are interdependent, it is necessary to determine how the parameters interact. In this section, the effects of various environmental and molecular parameters that impact the onset and rate of degradation are discussed.

Effect of temperature

The effect of temperature on the thermal degradation rates of polymers has been extensively explored because of the need to predict the service lifetime of consumer plastics. Elevated temperatures are used in these experiments to speed up the degradation of a plastic. Then, in order to determine the lifetime at more realistic temperatures (i.e. at lower temperatures more characteristic of the service temperatures), the assumption is made that an Arrhenius relationship holds. In contrast, only a few studies have probed the effect of temperature on the photochemical degradation rates of polymers. In brief, these studies are inconclusive and have not yielded a general model for predicting the dependence of photodegradation rates on temperature. Several studies found that quantum yields for photodegradation obey an Arrhenius relationship ($\phi = A\exp(-E_a/RT)$), but other studies found non-Arrhenius behavior (*33–37*). Several of these latter studies suggested that the non-Arrhenius behavior was due to the complexity of the degradation pathways discussed in the preceding sections. In general, interpreting the Arrhenius plots of photochemical reactions is non-trivial. In fact, Balzani noted that the relationship between the temperature and the activation parameters in any photochemical reaction is a complex one, and the "apparent activation energies" obtained from these studies should be interpreted with care (*38*).

The temperature can also impact the quantum efficiency of polymer photoreactions by causing changes in the molecular mobility of the polymer chains (which also leads to non-Arrhenius behavior) (*39–41*). One example is the photodegradation of poly(vinyl ketone) (PVK). Guillet and co-workers found that the quantum yields of degradation for PVK below the glass transition temperature, T_g, increased gradually with increasing temperature ($\Delta\Phi = 0.04$ for $T = 20 - 100°C$). To explain this behavior, Guillet noted that PVK degrades by a Norrish Type II mechanism, which proceeds via formation of a six-membered ring intermediate (Scheme 7). He proposed that, because the degradation pathway required substantial rearrangement of the polymer chain to form the six-membered ring intermediate, the slight increase in quantum yields with increasing temperature below T_g was a reflection of the slight increase in free-volume of the solid-state polymer. A larger free-volume allows for easier rearrangement of the chain to the six-membered ring intermediate. At T_g, the researchers observed a dramatic increase in the quantum yield to a value similar to that in solution ($\Phi_{PVK} = 0.24$). The sudden increase in Φ at the glass transition temperature was attributed to the ability of the polymer chains to easily form the reaction intermediate because of facile chain movement above T_g.

In another study, Daglen and Tyler studied the effect of temperature on the quantum yields for degradation of polymer **2** (*42*). They observed an exponential dependence (Figure 3), which they attributed to the temperature dependence of the diffusion apart of the two polymer fragments formed by photolysis in the degradation process (Scheme 8). It was noted that the polymer segments to which the radicals are attached are conformationally stressed. There are two possible modes for the newly formed radicals to relax and become separated: they can either rotate or recoil away from each other. These secondary motions of the polymer arise from the relaxation of unfavorable bond conformations that are formed during the polymer casting process. The increased thermal energy facilitates the rotation and



Scheme 7. Mechanism for the Norrish Type II photochemical reaction showing the formation of the six-membered ring intermediate.

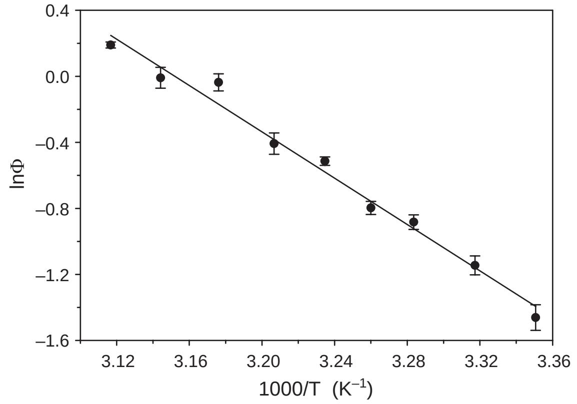


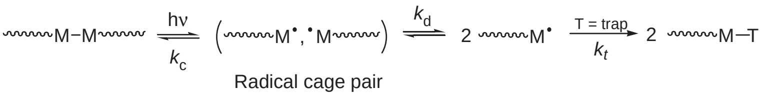
Figure 3. Plot of ln Φ versus T^{-1} for polymer **2**.
Source: See (*99*), Figure 2. With permission from Springer Science + Business Media.

recoil relaxation processes, which effectively increases the rate for diffusion of the radicals out of the cage formed by the surrounding molecules (Scheme 8). This leads to decreased radical–radical recombination and consequently an increase in photodegradation efficiency. The activation energy obtained from the lnΦ versus T^{-1} plot in Figure 3 is 14.1 ± 0.3 kcal mol^{-1}. This value is typical for secondary relaxation chain movements in polymers (which generally fall in the range 10–20 kcal mol^{-1} (*43–45*)) and is consistent with the proposal that the temperature dependence of Φ results from chain movements involved in recoil and rotation processes.

These findings can be summarized by stating that increasing the photoreaction temperature can have several effects (both direct and indirect) on the rate of polymer degradation. These effects include an increase in kinetic energy, in free-volume, and in molecular mobility. In addition, the ability of photogenerated radicals to diffuse apart has a temperature dependence, and this temperature dependence can also contribute to the overall temperature dependence of the degradation quantum yields. Finally, for photochemical reactions above T_g, chain mobility appears to be such that the quantum yields approachs those in solution.

Effect of radical trap concentration

The backbone degradation reactions that are integral to polymer degradation generally involve radical intermediates. As part of the degradation process, those radicals react with species that capture (trap) the radicals, which prevents a backreaction and thus leads to net degradation. The concentration of the trapping species will impact the degradation rates of polymers both in the solid-state and in solution. In the case of the autoxidative degradation pathway shown in Scheme 4, the carbon radical species that is formed in the initiation step must be trapped by an oxygen molecule for degradation to proceed. (The carbon radical could abstract a hydrogen atom from a C–H bond in lieu of reacting with oxygen but that would result in no net reaction or increase in the rate of the reaction.) In the solid-state, oxygen diffusion is often the rate-limiting step in the autoxidation of polymers. It was shown that rate-limiting oxygen diffusion is contingent on the sample thickness, morphology, and permeability of the polymer toward oxygen (*46,47*). Rate-limiting oxygen diffusion is also expected under experimental conditions where the light intensity is high relative to the rate at which oxygen is available to capture radicals. A specific example of rate-limiting oxygen diffusion comes from O'Donnell and White's study of the photochemical degradation of polystyrene (*48*). By sampling molecular weight as a function of depth, they found that the variation in polymer degradation with depth could not be explained by the difference in light intensity at the various depths or by variations in the tensile stress at the various depths. They concluded, rather, that oxygen depletion was responsible for the variation in degradation with depth, i.e. oxygen diffusion was rate-limiting. Their data showed that the degradation rate was oxygen limited even at a depth of only 100 μm from the surface. By fitting the data to an exponential function based on the so-called Zhurkov equation (*49*), they were able to estimate an activation free energy for the degradation process of 4.2 kJ mol^{-1}, a value consistent with the activation energy for small particle diffusion in a polymer matrix, i.e. a value consistent with rate-limiting oxygen diffusion. Interestingly, oxidative degradation was more prevalent at the corners of the samples. They hypothesized that oxygen has easier access to these regions of the sample because two surfaces are present rather than just one.



Scheme 8. Photochemical homolysis of a bond in a polymer and the subsequent trapping reaction depicting the caged radicals, where k_c is the rate constant for the geminate recombination, k_d is for diffusion from the radical cage, and k_t is for the radical trapping step.

For applications of rate-limiting oxygen diffusion to the design of degradable polymers, the general premise is that molecular diffusion is slower in crystalline regions than through amorphous regions. Therefore, samples with high fractional crystallinity should degrade slower than samples with smaller fractional crystallinity. As an example of this principle, Rabello and White (*50*) showed that fractional crystallinity was the main structural factor controlling the rate of polypropylene degradation. An interesting point, however, is that the diffusion of *all* molecules, not just oxygen, is hindered in crystalline material. By inhibiting the diffusion of the radical species involved in the termination steps of the autoxidation cycle, the kinetic chain length of the cycle will increase, with a resulting increase in the amount of oxidative degradation. Thus, as the fractional crystallization increases, two outcomes are possible: if oxygen diffusion is affected the most, and is therefore rate-limiting, then the rate of photo-oxidative degradation will decrease. If changes in the rate of the termination steps dominate then the rate of degradation will increase. Both cases have been observed experimentally. For a summary of examples where an increase in crystallinity leads to a decrease in the rate of degradation (*50*). Increases in degradation rates are found for the systems cited in references (*51–55*).

As a matter of practical application, the effect of decreased oxygen diffusion (caused by an increase in chain-order or crystallinity) is not always to decrease the rate of oxidative degradation. Most commercial polymers contain antioxidants, and the diffusion of these species will also decrease as ordering increases in the polymer. Their ability to act as antioxidants will thus also decrease. The net effect on the autoxidation process in these systems will be determined by which species, oxygen or antioxidant, is more affected by the decrease in diffusion.

Finally, the availability of oxygen in the interior of a polymer sample is also influenced by macroscopic structural features of the polymer. As a polymer degrades, cracks and fissures generally develop (initially on the surface), and their presence will facilitate penetration of oxygen into the interior (*56*). And, as discussed, the presence of corners will increase oxygen diffusion into a sample (*48*). Finally, it is noted that oxygen diffusion rates will be dependent on the oxygen partial pressure.

Effect of stress

An interesting outcome of artificial weathering studies on polymers is the finding that tensile and shear stresses can accelerate the rate of photodegradation (*57*). For example, recent studies of this phenomenon have shown that tensile stress will accelerate the degradation of numerous polyolefins (*48,56,58–69*), as well as polycarbonates (*60*), nylon (*70*), and acrylicmelamine coatings (*71,72*). Conversely, compressive stress (*59,73–75*) will generally retard photodegradation. These observations are of enormous practical importance because most polymers are subjected to light and some form of temporary or permanent stress during their lifetime. In order to control the onset of degradation and the rate of degradation in these materials, it is important to understand the mechanistic origins of the synergism between light and stress in these systems.

Mechanistic hypotheses to explain the effects of stress on photochemical degradation rates fall into three main categories (*24*). These categories are illustrated by reference to Scheme 9.

In one category, it is proposed that stress changes the quantum yields of the reactions that lead to bond photolysis, i.e. it is proposed that $\phi_{\mathrm{homolysis}}$ varies with stress. The second category attributes the variation in degradation rates with stress to changes in the efficiency of radical recombination following homolysis, i.e. $k_{\mathrm{recombination}}$ is proposed to depend on stress. And finally, the third category attributes the effects of stress to changes in the rate of the radical trapping reaction. (More detailed discussions of these three general categories have been presented elsewhere (*24*).)

Few studies have experimentally tested the various theories purporting to explain the origin of stress-dependent photodegradation rates. Those studies that have been done have generally been hampered by the mechanistic complexity of the degradation reactions (*76*). As discussed above, the photochemical degradation pathways generally involve multiple steps, cross-linking, and side-reactions; these features make pinpointing the origin of stress-induced rate accelerations difficult. Another formidable complication is that, as discussed in the preceding section, oxygen diffusion is the rate-limiting step in many photo-oxidative degradations (*77*). This adds to the intricacy of the analysis because oxygen diffusion rates are frequently time-dependent (*78,79*).

Work by Benachour and Rogers (*65*) provides an example of the complexity involved in the stress studies and of the interdependence of the various environmental and molecular parameters. In their first study, these workers studied the extent of

Scheme 9. A generalized reaction scheme showing photolysis of a bond along the backbone in a polymer (M represents a generic atom, carbon or otherwise).

oxidation in samples of irradiated polyethylene under stress. They observed that strain (caused by stress) initially caused an increase in the rate of oxidation but then a further increase in strain decreased the rate of oxidation. The explanation proposed was that stress (and strain) affected the rate of the radical trapping reaction due to changes in polymer morphology. In brief, the proposed explanation was that oxygen diffusion is facilitated at low stresses (because the sample is dilated) but inhibited (*64*) at higher stresses (because of increased chain ordering). In a subsequent study by Nguyen and Rogers (*80*), the oxidation behaviors of LDPE, polypropylene, and isotactic poly(1-butene) were investigated. In contrast to their earlier study (*65*), they found that the relative oxidation rate decreased slightly at very low strains before increasing at higher strains. The explanation offered for the behavior at very low strains was that strain initially causes an increase in chain order, which results in a decrease in the oxygen diffusion rate. Taken together, these two studies by the Rogers group suggest that the effect of stress on a polymer sample undergoing photo-oxidation is the following: (1) very low stress increases ordering in the amorphous chains, which decreases oxygen diffusion, which in turn decreases oxidation and hence degradation rate; (2) higher stress dilates the polymer (and stresses the bonds in the chains), which increases oxygen diffusion, which in turn increases oxidation; and (3) yet higher stress orders the chains and increases crystallinity, which decreases oxygen diffusion, which in turn decreases oxidation. The general applicability of these results is hampered by the lack of other quantitative studies.

In other work, Tyler and Chen studied the effect of tensile stress on the photochemical degradation efficiency of polymer **2** (*24,81*). When irradiated with visible light, this polymer photodegraded, even in the absence of oxygen. Infrared spectroscopic analysis demonstrated that the chlorine atoms along the polymer backbone act as built-in traps for Mo-centered radicals formed by photolysis of the Mo–Mo bonds. The presence of the internal radical trap permitted the polymer samples to be irradiated in the absence of oxygen, thus eliminating the kinetically complicating effects of rate-limiting oxygen diffusion. Results showed that stress initially increased the quantum yields for degradation but the quantum yields reached a maximum value and then decreased with higher stress. These results are consistent with the hypothesis that attributes the effects of stress to changes in $k_{\text{recombination}}$, i.e. the function of stress is to increase the initial separation of the photochemically generated radical pair, which has the effect of decreasing their recombination efficiency and thus increasing the degradation efficiency. This hypothesis predicts an eventual downturn in degradation efficiency, as was observed in this study, because the polymer chain becomes ordered at high stress; the increased order hinders diffusion apart of the radicals and thus increases their probability of recombination. Wide angle X-ray diffraction and infrared spectroscopy confirmed that chain orientation increased with increasing stress on polymer **1**.

One final example of the stress/morphology/degradation-rate interaction is Rapoport's study of polypropylene (*82,83*), which showed that oriented chains of this polymer were less susceptible to oxidation because they had an unfavorable conformation for participation in the autoxidation reaction relative to amorphous chains. Stress and chain-orientation effects work both ways, however. The work of Bellinger on PVC is frequently cited as an example where stress induces a chain orientation that is *more* favorable for degradation, apparently because of a chain conformation that is more susceptible to hydrogen abstraction (*84*).

In summary of this section, the following equation shows the relationship between stress, polymer morphology, and degradation rates:

$$\text{Stress} \xrightarrow{\text{Affects}} \text{Morphology} \xrightarrow{\text{Affects}} \text{Degradation rate.} \quad (2)$$

Tensile or shear stress will: (1) first stretch the chains in an amorphous region of a polymer sample; (2) then order those polymer chains; and (3) then induce crystallinity in those regions of the polymer. These changes will affect chemical reactivity because molecular diffusion is slower in ordered and crystalline phases compared to amorphous phases (*73*); consequently, intermolecular reaction rates, such as those in the autoxidation cycle, will be slower in ordered polymers. In attempting to generalize these results to other polymers, it is prudent to be cautious. For example, in a photo-oxidation reaction, the downturn in efficiency with higher stress may be caused by the development of microcracks and fissures, which act to release the stress. Or, perhaps the microcracks and fissures can act as channels for oxygen, which will increase the rate of degradation. We are a ways off before these findings can be incorporated into design features that can specifically account for the effects of stress on polymer degradation rates.

Kinetic models of polymer photodegradation

A typical first step in the analysis of photochemically induced polymer degradation is to determine the kinetics of the degradation reaction. An interesting observation from kinetic studies of the photodegradation rates of solid-state polymers is that the plots of degradation versus irradiation time are often biphasic, showing a relatively fast rate constant during the initial period of irradiation but a smaller rate constant at longer times (*32,85*). For completeness, it is noted that traditional zero-order, first-order, or second-order kinetics are also sometimes observed for polymer degradation reactions. For example, zero-order kinetics, which are typical for many photochemical reactions, are observed when the absorbance is very high. Photo-oxidative degradation in the presence of excess oxygen has been shown in several cases to exhibit first-order kinetics (*86–89*). In all such cases, which include polyethers, conjugated polymers, and poly(vinyl chloride), the main chain scission results from formation of a carboxyl carbon, usually an ester linkage, which is subsequently involved in β-scission. Second-order kinetics in polymer photodegradation are less prevalent in the literature. To site one example, second-order kinetics were observed for the photodegradation of neoprene in the presence of $FeCl_3$ (*90*). However, no definitive explanation was offered as to the origin of this behavior.

A study by Daglen and Tyler showed that biphasic kinetics behavior in the photochemical degradation of polymers can be explained by so-called Perrin kinetics (*91*). These kinetics apply when a chemical species is converted to a single product in the same reaction vessel by two or more mechanistically different routes that possess different observed rates. The Perrin model, shown in Figure 4, was first proposed in the early twentieth century to explain the observed non-exponential fluorescence decay of small molecules in solid polymers (*92,93*). Perrin considered the micro-heterogeneity of solid-state polymers and the relative immobility of atoms in the solid-state. For fluorescence decay, he proposed that when an acceptor was in the quenching sphere of an electronically excited donor molecule, the fluorescence would be quenched. Therefore, the observed rate of fluorescence decay was the combination of the decay rate of excited molecules in the presence of a quencher and the natural decay rate of molecules in the absence of a quencher. A mechanistic analogy can be made for photogenerated radical species in solid-state polymers: the observed rate of radical decay will be the combination of the rate where a radical trapping agent is in the reactive sphere of the radical and where it is not (the term “reactive sphere” is equivalent to the term “quenching sphere” used in the case of the original Perrin model). This is represented pictorially in Figure 4(a) and (b). The appropriate equation to describe Perrin-like kinetics is shown in Equation (3). This equation was shown to give excellent fits to the degradation kinetics of polymers (*91*):

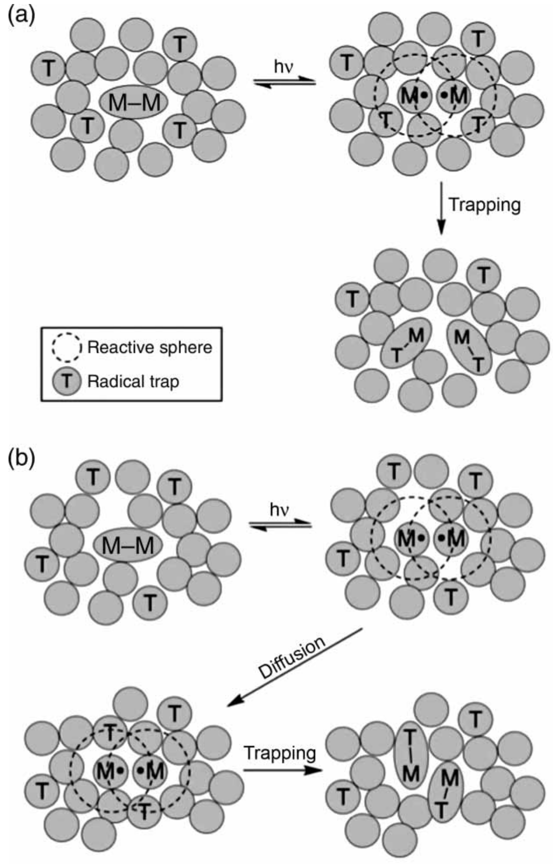


Figure 4. Illustration of the reaction of photogenerated metal radicals with trapping atoms in a solid-state matrix. In case (a) there is a trap in the reactive sphere of the metal radical and (b) the trap is initially outside of the reactive sphere.

$$[A] = X_0 + k_1 t + Y_0 e^{-k_2 t}. \qquad (3)$$

An investigation of temperature effects on the parameters extracted from the fits to the Perrin-like model showed that only a few percent of the radical species generated had radical trapping agents in the reactive sphere (Perrin-like environment) and that the majority of metal radicals did not have radical trapping agents in the reactive sphere (diffusive environment). It was also found that the apparent $\Delta H^{\ddagger}$ for the photoreaction in the Perrin-like environment was lower than that of the diffusive reaction. It was hypothesized that the rate-limiting step in the diffusive reaction is diffusion together of the photogenerated radical and the radical trapping agent.

In summary, understanding the kinetics of degradation is one of the keys to designing viable photochemically degradable plastics. The Perrin model adequately describes the kinetics of polymer degradation in those cases where biphasic behavior is observed.

Absorbed light intensity

Light intensity effects on polymer reactions are generally analogous to the "dose rate" effects seen in γ irradiation experiments (*94*). In general, an increase in the absorbed light intensity will increase the rate of a photochemical reaction. (To visualize why this is so, consider the photon as a reagent (*93*). An increase in the number of photons striking the polymer per unit time, i.e. an increase in the absorbed intensity, will increase the rate of the photochemical step in the same way that increasing the concentration of a reagent will increase the rate of an elementary step. Although saturation can occur with chemical reagents, saturation rarely occurs with photons unless lasers or exceptionally high-intensity lamps are used as the light source. Note that only "absorbed" photons can cause photochemical reactions (*95*). Hence, rate laws and quantum yield expressions use the absorbed intensity (generally abbreviated I_a) and not merely the intensity (I).) To normalize for the effect of the absorbed light intensity, photochemists use the concept of the "quantum yield," which is defined as the rate of the reaction divided by the absorbed light intensity. Thus, although light intensity will generally affect the rate of polymer degradation, the quantum yield (also called the "quantum efficiency") will generally not be affected by intensity.

There are well-established instances, however, where the quantum yield of a photochemical reaction can be affected by the light intensity. A specific case in point, relevant to polymer degradations, occurs in those pathways where two photochemically generated intermediates, such as radicals, can react. In such instances, the rate of the elementary reaction involving the two intermediates will be proportional to the square of the intermediates' concentration, i.e. rate $\propto$ [intermediate]^2. Such bimolecular reactions would typically be termination steps in, say, a radical polymerization reaction. If this reaction is in competition with other reactions of the intermediates involving rates that are first-order in intermediate concentration, then the second-order reaction will increase in rate *relative to* the first-order reactions as the concentration of the intermediate increases. In general, intermediates increase in concentration as the light intensity increases. Thus, in this example, the quantum yield would drop as the light intensity increased because the termination step increases in efficiency relative to the propagating steps (note, however, that the *rate* of the overall reaction would likely still increase as the light intensity increased).

Polymer morphology

There is general agreement that polymer morphology is a parameter that has an extremely important influence on the rate of polymer photochemical degradation reactions (*50,52,53,96*). For example, as discussed above, polymer morphology is one of the keys to interpreting the effect of stress on degradation rates because stress affects the morphology and morphology affects the degradation rates. In another example, Rabello and White probed the role of morphology in the photochemical degradation of polypropylene (*50*). They found that samples with higher fractions of crystallinity degraded slower than samples with less crystallinity (for sample exposure times of at least 12 weeks; for short exposure times there was no correlation between fractional crystallinity and extent of degradation). Their explanation was that oxygen diffusion is slower in the crystalline regions.

Cross-linking can also affect photodegradation rates by "locking" the polymer structure and preventing lamellar unfolding. The consequence is to prevent separation of photo-produced radicals, which thus favors radical–radical combination. Crosslinked systems therefore generally have smaller quantum yields of degradation relative to non-crosslinked systems (*62*).

Chromophore concentration

As the final point for discussion, it is noted that chromophore concentration can affect the rate of a photochemical reaction (*97,98*) (as used here and in the literature, "chromophore" refers to any functional group, whether intentionally present or not, that absorbs light. Examples of adventitious chromophores include the hydroperoxy, carbonyl, and hydroxy groups that form in the autoxidation cycle.) If a polymer has a higher concentration of chromophores, its degradation rate will be faster simply because more sites are available to absorb photons and initiate a reaction. An example of this phenomenon is found with the E-CO polymers, where a higher concentration of carbonyl groups was shown to give higher backbone fragmentation rates (*7*). The quantum yield of the reaction will not change, however, because the quantum yield is the reaction rate normalized by the intensity of the absorbed light. Recall, however, that quantum yields can be intensity dependent if the reaction mechanism involves first-order propagating steps in competition with second-order termination steps.

Conclusions and summary of the design principles

As discussed, the ideal photochemically degradable polymer will have an onset of degradation that is reliably predictable. In addition, the onset of degradation will be tunable and the degradation, once started, will proceed quickly. Although there is still much to learn, a number of principles are beginning to emerge for the design of viable photochemically degradable plastics.

- *The chromophore*. Photodegradable polymers are typically made by either incorporating a chromophore into the polymer backbone (or as a side-chain) or by deliberate addition of a chromophore additive that photochemically generates radicals, which starts the autoxidation cycle. In practice, the chromophore incorporated into the backbone most often is CO, but in principle other chromophores will also work. Degradation then occurs by photochemical Norrish Types I and II reactions. No chromophore yet devised can control the onset of degradation by itself.
- *Controlling the onset of degradation*. The onset of degradation can be controlled by adding an initiator (a photochemical initiator in the case of a photochemically degradable plastic) and an antioxidant. As long as both additives are present, degradation will be minimized. But, if slightly more initiator is present then eventually, when the antioxidant has all been consumed, oxidative degradation will start. The lifetime of the plastic can be controlled by adjusting the relative amounts of the antioxidant and the initiator.
- *Temperature effects*. The effect of temperature on a photochemical reaction is complex. In general, as the temperature increases the rate of degradation will increase. In some cases, an Arrhenius relationship is observed but in others it is not. Studies suggest that if the quantum efficiency of the photodegradation is controlled by the "cage effect" (i.e. by the ability of a radical pair to diffuse apart and escape each other) then the relationship between the quantum yield and temperature may generally be governed by the Arrhenius equation. However, if the quantum efficiency is governed by the mobility of the polymer chains then non-Arrhenius behavior is expected. At present, it is safe to say that the temperature dependence of photodegradation for any new polymer must be determined empirically.
- *Radical trap concentration*. Whether photochemical or thermal, most polyolefin degradation reactions begin by the formation of radicals, which go on to react in an autoxidation cycle. Oxygen is a critical component in this cycle and its concentration will effect the overall rate of degradation. In many instances, the rate-limiting step is oxygen diffusion. Studies showed that rate-limiting oxygen diffusion is contingent on sample thickness, morphology, and permeability of the polymer to oxygen. Rate-limiting oxygen diffusion is also expected under experimental conditions where the light intensity is high, relative to the rate at which oxygen is available to capture radicals.
- *Polymer morphology*. For applications of rate-limiting oxygen diffusion to the design of degradable polymers, the general premise is that molecular diffusion is slower in crystalline regions than through amorphous regions. An increase in crystallinity will increase the rate of degradation, however, if the rate of degradation is determined by the rate of the termination steps (radical–radical coupling or disproportionation). The diffusion of antioxidants is inhibited in crystalline polymers, and so an increase in crystallinity may increase the degradation rates of more highly crystalline polymers.
- *Stress*. Tensile stress will increase the rate of polymer degradation, up to a point, and then start to decrease the rate. Compressive stress will decrease the rate of polymer degradation. These observations are important because plastic items are generally under some type of residual stress from the manufacturing process. This stress must be accounted for in determining the onset and rate of photodegradation.
- Two last parameters that can effect the photochemical degradation rates of polymers are the *absorbed light intensity* and the *chromophore concentration*. (These two are related: a higher chromophore concentration leads to more light absorption.) The chromophore concentration can be controlled in the design process, but the light intensity will vary with location. One design possibility is to adjust the chromophore concentration according to where the degradable plastic will be used. For example, a plastic to be used in the sunny American Southwest might have less chromophore than a plastic to be used in the overcast Pacific Northwest.

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References

(1) Anastas, P.T.; Williamson, T.C., Eds. *Green Chemistry: Frontiers in Benign Chemical Syntheses and Processes*; Oxford University Press: New York, 1998.

(2) Thomas, R.; Dexter, M.; King III, R.E. *Kirk-Othmer Encyclopedia of Chemical Technology*, 5th ed.; Wiley - Interscience, New Jersey, 2004; Vol. 3, pp 102–134.

(3) Scott, G. *Polymers and the Environment;* Royal Society of Chemistry: Cambridge, UK, 1999.

(4) Scott, G.; Gilead, D., Eds. *Degradable Polymers: Principles and Applications*, 2nd ed.; Chapman & Hall: New York, 2002.
(5) Vilaplana, F.; Karlsson, S. *Macromol. Mater. Eng.* **2008,** *293*, 274–297.
(6) See the Association of Postconsumer Plastic Recyclers Design for Recyclability Program on the web. http://www.plasticsrecycling.org/technical_resources/design_for_recyclability_guidelines/index.asp (accessed July 14, 2009).
(7) Scott, G. *Trends Polym. Sci.* **1997,** *5*, 361–368.
(8) Grassie, N.; Scott, G. *Polymer Degradation and Stabilization*; Cambridge University Press: New York, 1985.
(9) West, R.; Maxka, J. *ACS Symp. Ser.* **1988,** *360*, 6–20.
(10) West, R. *J. Organomet. Chem.* **1986,** *300,* 327–346.
(11) Wiles, D.M.; Scott, G. *Polym. Degrad. Stab.* **2006,** *91*, 1581–1592.
(12) Steber, J.; Herold, C.P.; Limia, J.M. *Chemosphere* **1995,** *31*, 3105–3118.
(13) Albertsson, A-C.; Barenstedt, C.; Karlsson, S.; Lindberg, T. *Polymer* **1995,** *36*, 3075–3083.
(14) Guillet, J. *Polymer Photophysics and Photochemistry: An Introduction to the Study of Photoprocesses in Macromolecules*; Cambridge University Press: New York, 1985.
(15) Sommazzi, A.; Garbassi, F. *Prog. Polym. Sci.* **1997,** *22*, 1547–1605.
(16) Hartley, G.H.; Guillet, J.E. *Macromolecules* **1968,** *1*, 413–417.
(17) Hartley, G.H.; Guillet, J.E. *Macromolecules* **1968,** *1*, 165–170.
(18) Schnabel, W. *Polymers and Light: Fundamentals and Technical Aspects*; Wiley-VCH: Weinheim, 2007.
(19) Hocking, P.J. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **1992,** C32, 35–54.
(20) Tyler, D.R. *Coord. Chem. Rev.* **2003,** *246*, 291–303.
(21) Meyer, T.J.; Caspar, J.V. *Chem. Rev.* **1985,** *85*, 187–218.
(22) Geoffroy, G.L.; Wrighton, M.S. *Organometallic Photochemistry;* Academic Press: New York, 1979.
(23) Tenhaeff, S.C.; Tyler, D.R. *Organometallics* **1991,** *10*, 473–482.
(24) Chen, R.; Tyler, D.R. *Macromolecules* **2004,** *37*, 5430–5436.
(25) Rabek, J.F. *Photodegradation of Polymers Physical Characteristics and Applications*; Springer: New York, 1996.
(26) Kaczmarek, H. *Curr. Top. Polym. Res.* **2005,** 71–124.
(27) Roy, P.K.; Surekha, P.; Rajagopal, C.; Choudhary, V. *J. Appl. Polym. Sci.* **2008,** *108*, 2726–2733.
(28) Amin, M.U.; Scott, G. *Eur. Polym. J.* **1974,** *10*, 1019–1028.
(29) Mellor, D.C.; Moir, A.B.; Scott, G. *Eur. Polym. J.* **1973,** *9*, 219–225.
(30) Xu, J.; Shi, W.; Gong, M.; Yu, F.; Yan, L. *J. Appl. Polym. Sci.* **2005,** *97*, 1714–1724.
(31) Matsukawa, K. *J. Photopolym. Sci. Technol.* **2005,** *18*, 203–210.
(32) Hwu, J.R.; King, K.Y. *Chem. Eur. J.* **2005,** *11*, 3805–3815.
(33) Yamashita, T.; Tomitaka, H.; Kudo, T.; Horie, K.; Mita, I. *Polym. Degrad. Stab.* **1993,** *39*, 47–54.
(34) Mishra, R.; Tripathy, S.P.; Fink, D.; Dwivedi, K.K. *Radiat. Eff. Defects Solids* **2004,** *159*, 569–573.
(35) Mishra, R.; Tripathy, S.P.; Fink, D.; Dwivedi, K.K. *Radiat. Meas.* **2005,** *40*, 754–757.
(36) Celina, M.; Gillen, K.T.; Assink, R.A. *Polym. Degrad. Stab.* **2005,** *90*, 395–404.
(37) Audouin, L.; Girois, S.; Achimsky, L.; Verdu, J. *Polym. Degrad. Stab.* **1998,** *60*, 137–143.
(38) Balzani, V.; Carassiti, V. *Photochemistry of Coordination Compounds;* Academic Press: New York, 1970.
(39) Yoshioka, T.; Saitoh, N.; Okuwaki, A. *Chem. Lett.* **2005,** *34*, 70–71.
(40) Boxhammer, J. *Polym. Test.* **2001,** *20*, 719–724.
(41) Feller, R.L.; Curran, M.; Colaluca, V.; Bogaard, J.; Bailie, C. *Polym. Degrad. Stab.* **2007,** *92*, 920–931.
(42) Daglen, B.C.; Harris, J.D.; Tyler, D.R. *J. Inorg. Organomet. Poly. Mater.* **2007,** *17*, 267–274.
(43) Fried, J.R. *Polymer Science and Technology,* 1st ed.; Prentice Hall PTR: Upper Saddle River, NJ, 1995.
(44) Elicegui, A.; Del Val, J.J.; Millan, J.L.; Mijangos, C. *J. Non-Cryst. Solids* **1998,** *235–237*, 623–627.
(45) David, L.; Girard, C.; Dolmazon, R.; Albrand, M.; Etienne, S. *Macromolecules* **1996,** *29*, 8343–8348.
(46) Pospisil, J.; Pilar, J.; Billingham, N.C.; Marek, A.; Horak, Z.; Nespurek, S. *Polym. Degrad. Stab.* **2006,** *91*, 417–422.
(47) Le Huy, H.M.; Bellenger, V.; Paris, M.; Verdu, J. *Polym. Degrad. Stab.* **1991,** *35*, 171–179.
(48) O'Donnell, B.; White, J.R. *J. Mater. Sci.* **1994,** *29*, 3955–3963.
(49) Zhurkov, S.N.; Zakrevskii, V.A.; Korsukov, V.E.; Kuksenko, V.S. *J. Polym. Sci. Polym. Phys. Ed.* **1972,** *10*, 1509–1520.
(50) Rabello, M.S.; White, J.R. *Polym. Degrad. Stab.* **1997,** *56*, 55–73.
(51) Rapoport, N.Y.; Berulava, S.I.; Kovarskii, A.L.; Musaelyan, I.N.; Ershov, Y.A.; Miller, V.B. *Vysokomol. Soedin. Ser. A* **1975,** *17*, 2521–2527.
(52) Dogue, L.J.; Mermilliod, N.; Genoud, F. *J. Polym. Sci. Part A Polym. Chem.* **1994,** *32*, 2193–2198.
(53) Billingham, N.C.; Prentice, P.; Walker, T.J. *J. Polym. Sci. Polym. Symp.* **1977,** *57*, 287–297.
(54) Akay, G.; Tincer, T.; Aydin, E. *Eur. Polym. J.* **1980,** *16*, 597–600.
(55) Slobodetskaya, E.M. *Usp. Khim.* **1980,** *49*, 1594–1616.
(56) Schoolenberg, G.E.; Vink, P. *Polymer* **1991,** *32*, 432–437.
(57) White, J.R.; Rapoport, N.Y. *Trends Polym. Sci.* **1994,** *2*, 197–202.
(58) O'Donnell, B.; White, J.R. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1993,** *34*, 137–138.
(59) Tong, L.; White, J.R. *Polym. Degrad. Stab.* **1996,** *53,* 381–396.
(60) Kelly, C.T.; Tong, L.; White, J.R. *J. Mater. Sci.* **1997,** *32*, 851–861.

(61) O'Donnell, B.; Qayyum, M.M.; Tong, L.; White, J.R. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1993,** *34*, 211–212.
(62) Busfield, W.K.; Monteiro, M. *J. Mat. Forum* **1990,** *14*, 218–223.
(63) Baumhardt-Neto, R.; De Paoli, M.A. *Polym. Degrad. Stab*. **1993,** *40*, 59–64.
(64) Baumhardt-Neto, R.; De Paoli, M.A. *Polym. Degrad. Stab*. **1993,** *40*, 53–58.
(65) Benachour, D.; Rogers, C.E. *ACS Symp. Ser*. **1981,** *151*, 263–274.
(66) Igarashi, M.; DeVries, K.L. *Polymer* **1983,** *24*, 1035–1041.
(67) Huvet, A.; Philippe, J.; Verdu, J. *Eur. Polym. J*. **1978,** *14*, 709–713.
(68) Busfield, W.K.; Taba, P. *Polym. Degrad. Stab*. **1996,** *51*, 185–196.
(69) Thominette, F.; Verdu, J. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1994,** *35*, 971–972.
(70) Igarashi, M.; DeVries, K.L. *Polymer* **1983,** *24*, 769–782.
(71) Nguyen Truc Lam, H.; Rogers, C.E. *Polym. Mater. Sci. Eng*. **1987,** *56*, 589–592.
(72) Appleby, R.W.; Busfield, W.K. *J. Mater. Sci*. **1994,** *29*, 151–156.
(73) Popov, A.; Rapoport, N.; Zaikov, G. *Oxidation of Stressed Polymers;* Gordon and Breach Science: New York, 1991.
(74) DeVries, K.L.; Hornberger, L.E. *Polym. Degrad. Stab*. **1989,** *24*, 213–240.
(75) Popov, A.A.; Blinov, N.N.; Krisyuk, B.E.; Zaikov, G.E. *Polym. Degrad. Stab*. **1984,** *7*, 33–39.
(76) Geuskens, G. *Compr. Chem. Kinet*. **1975,** *14*, 333–424.
(77) Audouin, L.; Langlois, V.; Verdu, J.; de Bruijn, J.C.M. *J. Mater. Sci*. **1994,** *29*, 569–583.
(78) Cunliffe, A.V.; Davis, A. *Polym. Degrad. Stab*. **1982,** *4*, 17–37.
(79) Malik, J.; Hrivik, A.; Tuan, D.Q. *Adv. Chem. Ser*. **1996,** *249*, 455–471. See page 459 in particular.
(80) Nguyen, T.L.; Rogers, C.E. *Polym. Mater. Sci. Eng*. **1985,** *53*, 292–296.
(81) Chen, R.; Yoon, M.; Smalley, A.; Johnson, D.C.; Tyler, D.R. *J. Am. Chem. Soc*. **2004,** *126*, 3054–3055.
(82) Rapoport, N.Y.; Zaikov, G.E. *Eur. Polym. J*. **1984,** *20*, 409–414.
(83) Rapoport, N.Y.; Shibryaeva, L.S.; Zaikov, V.E.; Iring, M.; Fodor, Z.; Tudos, F. *Polym. Degrad. Stab*. **1985,** *12*, 191–202.
(84) Bellenger, V.; Verdu, J.; Martinez, G.; Millan, J. *Polym. Degrad. Stab*. **1990,** *28*, 53–65.
(85) Rivaton, A.; Gardette, J-L.; Mailhot, B.; Morlat-Therlas, S. *Macromol. Symp*. **2005,** *225*, 129–146.
(86) Fraisse, F.; Morlat-Therias, S.; Gardette, J.L.; Nedelec, J.M.; Baba, M. *J. Phys. Chem. B* **2006,** *110*, 14678–14684.
(87) Bigger, S.W.; Delatycki, O. *J. Polym. Sci. Part A Polym. Chem*. **1987,** *25*, 3311–3323.
(88) Sarkas, H.W.; Kwan, W.; Flom, S.R.; Merritt, C.D.; Kafafi, Z.H. *J. Phys. Chem*. **1996,** *100*, 5169–5171.
(89) Ivanov, V.B.; Zhuravlev, M.A. *Polym. Photochem*. **1986,** *7*, 55–64.
(90) Freitas, A.R.; Vidotti, G.J.; Rubira, A.F.; Muniz, E.C. *Polym. Degrad. Stab*. **2005,** *87*, 425–432.
(91) Daglen, B.C.; Tyler, D.R. *Macromolecules* **2008,** *41*, 9525–9531.
(92) Perrin, F. *Compt. Rend*. **1924,** *178*, 1978–1980.
(93) Turro, N.J. *Modern Molecular Photochemistry;* Addison-Wesley: Reading, MA, 1978.
(94) Barron, P.F.; Busfield, W.K.; Hanna, J.V. *Polym. Commun*. **1988,** *29*, 70–72.
(95) Calvert, J.G.; Pitts, J.N. *Photochemistry;* Wiley: New York, 1966.
(96) Ogier, L.; Rabello, M.S.; White, J.R. *J. Mater. Sci*. **1995,** *30*, 2364–2376.
(97) Carlsson, D.J.; Wiles, D.M. *J. Macromol. Sci. Rev. Macromol. Chem*. **1976,** *C14*, 65–106.
(98) Garton, A.; Carlsson, D.J.; Wiles, D.M. *J. Polym. Sci. Polym. Chem. Ed*. **1978,** *16*, 33–40.
(99) Daglen, B.C.; Harris, J.D.; Tyler, D.R. Factors Controlling the Rate of Photodegradation in Polymers: The Effect of Temperature on the Photodegradation Quantum Yield in a PVC Polymer Containing Metal–Metal Bonds in the Polymer Chain. *J. Inorg. Organomet. Polym. Mater*. **2007**, *17*, 267–274.