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Photochemically Degradable Polymers Containing Metal-Metal Bonds along Their Backbones: The Effect of Stress on the Rates of Photochemical Degradation

David R. Tyler, Rui Chen*

Department of Chemistry, University of Oregon, Eugene, OR 97403 USA
E-mail: dtyler@uoregon.edu

Summary: The syntheses of polymers that have metal-metal bonds along their backbones are described. The polymers are photodegradable because the metal-metal bonds homolyze when irradiated with visible light. The photochemical reactions of the polymers in solution are identical to the photochemical reactions of the discrete metal-metal bonded dimers. Typical reactions include metal-metal bond disproportionation and metal radical capture, for example, by chlorine atom abstraction from carbon tetrachloride. The polymers are also photochemically degradable in the solid state; thin films of the polymers degrade when irradiated with visible light in the presence of oxygen or in the absence of oxygen if the polymer backbone has a built-in radical trap. The origin of tensile stress-induced rate enhancements in the photodegradation of polymers was studied using the polymers with metal-metal bonds along their backbones and with built-in radical traps. By eliminating the need for external oxygen to act as a radical trap, the experimentally challenging problem of diffusion-controlled oxidation kinetics was avoided. Analysis of plots of quantum yields for degradation vs. stress reveals that stress increases the separation of the radical fragments produced by photolysis. An increased separation leads to less radical-radical recombination, which increases the efficiency of degradation. Quantitative knowledge of the factors that control polymer degradation rates will eventually allow synthesis of an ideal photodegradable polymer - one that has a tunable onset of degradation and that degrades quickly once degradation has started.

Keywords: metal-metal bonds; metal-polymer complexes; photochemical degradation; photochemistry; stress

Introduction

An interesting outcome of artificial weathering studies on polymers is the finding that tensile- and shear-stress can accelerate the rate of photodegradation.[1] Recent studies of this phenomenon have shown that stress will accelerate the photo-oxidative degradation of many

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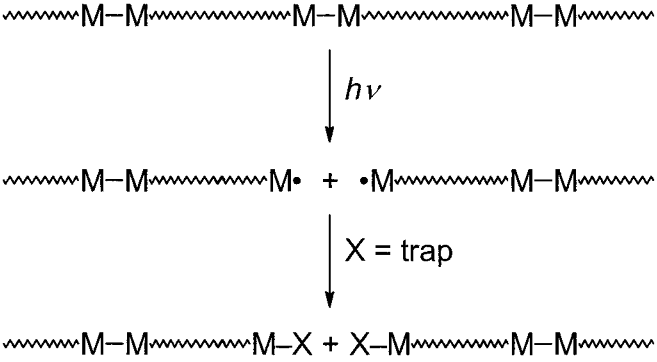
polyolefins, including polystyrene,[2,3] polypropylene,[4-9] polyethylene,[10-13] polyethylene/ polypropylene copolymer,[14] and PMMA,[15] as well as polycarbonates,[8] nylon,[16] and acrylic-melamine coatings.[17] These findings are of enormous practical importance because most polymers are subjected to light and some form of temporary or permanent stress during their lifetime. It is thus important to find ways to control the enhanced degradation induced by the synergism of light and stress. In contrast, some polymers are designed to degrade when exposed to light. In order to control the onset of degradation and the rate of degradation in these materials, it is likewise important to understand the mechanistic origins of the synergism between light and stress in these systems. Our research is aimed at finding answers to two intriguing questions of scientific and practical concern: *why does stress cause changes in the photodegradation rate* and *what is the quantitative relationship between stress and the rate of photodegradation*? To answer these questions, we conceived and synthesized a new class of polymers containing metal-metal bonds along their backbones. This paper provides an overview of these new materials and it reports the results of our investigation on the effect of stress on photochemical degradation rates of polymers.

Background

A Workable Experimental Approach to the Problem

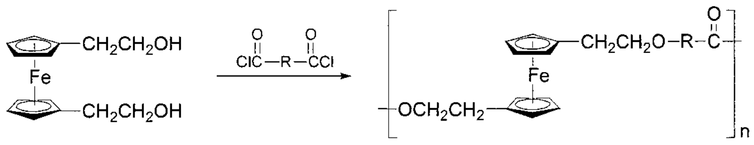
Very little is known about the quantitative relationship of stress to photochemical degradation rates. One of the reasons so little is known is that polymer degradations are mechanistically complicated.[18] This is not to say that the mechanisms are not understood; in fact, they are understood in detail.[18] Rather, the mechanisms are intricate, often involving multiple steps, cross-linking, and side-reactions; this makes pinpointing the effects of stress difficult. For example, one formidable complication is that oxygen diffusion is the rate-limiting step in many photooxidative degradations.[13],[19] This adds to the intricacy of the analysis because oxygen diffusion rates are frequently time-dependent.[19,20] To circumvent these experimental and mechanistic complexities and therefore make it less difficult to interpret data and obtain fundamental insights, we use three key experimental strategies in our study of stress effects on photodegradation. First, we study the problem using photodegradable polymers that contain metal-metal bonds along the backbone.[21-26] These polymers degrade with visible light by a straightforward mechanism involving metal-metal bond homolysis followed by capture of the metal radicals with an appropriate radical trap (typically either oxygen or an organic halide; Scheme 1). By studying the effect of stress on these "model" systems, we can extract information without the mechanistic complications inherent in the degradation mechanisms of organic radicals. (For example, metal radicals do not lead to crosslinking, so we can avoid this complicating feature found with organic radicals.) The second key experimental strategy is to use polymers that have built-in radical traps. By eliminating the need for external oxygen to act as a trap, we can exclude the complicating kinetic features of diffusion-controlled oxidation reactions. The third experimental strategy is to use the distinctive M-M bond chromophore to monitor spectroscopically the polymer photodegradations and to obtain quantum yields. Typically, degradation reactions are monitored by stress testing, molecular weight measurements, or attenuated total reflection (ATR) spectroscopy, all of which can be laborious and time consuming. Quantum yields on thin film polymer samples are easily measured in our lab with a computerized apparatus, and progress is expedited accordingly.



Scheme 1. Photochemical degradation of a polymer with metal-metal bonds along its backbone

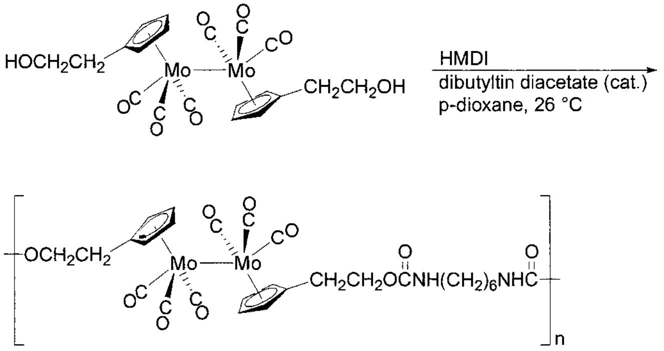
Synthesis and Characterization of the Photodegradable Polymers

Our general synthetic route for incorporating metal-metal bonds into polymer backbones is based on the step polymerization techniques for incorporating ferrocene into polymer backbones.[27-33] Step polymers of ferrocene can be made by substituting the Cp rings with appropriate functional groups, followed by reaction with appropriate difunctional organic monomers (e.g., Equation 1).[34-36]



(1)

The analogous strategy for synthesizing metal-metal bond-containing polymers also uses difunctional, cyclopentadienyl-substituted metal dimers. A sample polymerization reaction is shown in Equation 2, which illustrates the reaction of a metal-metal bonded "diol" with hexamethylene diisocyanate (HMDI) to form a polyurethane.[21]



(2)

This step polymerization strategy is quite general, and a number of metal-metal bond-containing polymers have been made from monomers containing functionalized Cp ligands.[27-33, 37]

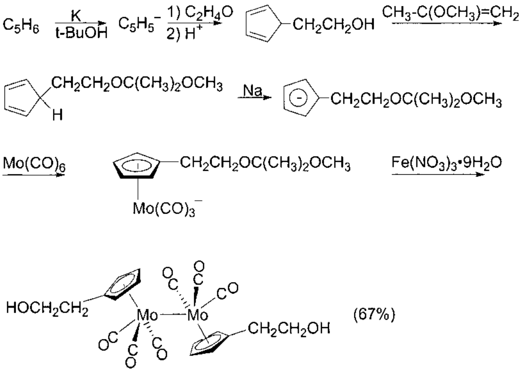
Synthesis of the Difunctional Dimers

The essential starting materials in the synthesis of the metal-metal bond-containing polymers are metal-metal bonded dimers with functional groups substituted on the Cp rings. The metal-metal bonds are relatively weak, and therefore they will not stand up to the harsh conditions typically required for the substitution of metal-coordinated Cp rings. For this reason, it is necessary to synthesize first the substituted cyclopentadienyl ligands and then coordinate these rings to the metals. A high yield synthetic route to the alcohol-substituted Cp rings is summarized in

Scheme 2. The syntheses of other substituted dimers are detailed in references.[21-23] A sample route to the difunctional dimer molecule is also shown in Scheme 2. Note that the general route shown for the Mo-containing dimers (involving Fe^{3+} oxidation of the anionic species) was developed by Manning.[38, 39]

Synthesis of the Polymers

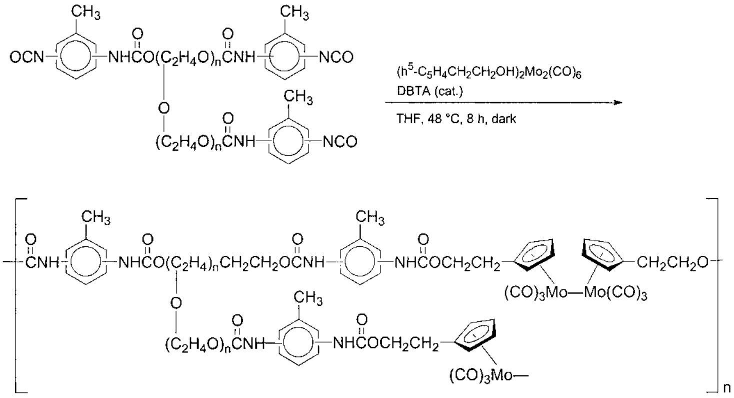
Just as the comparatively weak metal-metal bonds pose problems for the synthesis of the difunctional dimers, they cause similar problems in the synthesis of the polymers. The relative weakness of the metal-metal bonds makes them more reactive than the bonds found in standard organic polymers; thus, under many standard polymerization reaction conditions, metal-metal bond cleavage would result. For example, metal-metal bonds react with acyl halides to form metal halide complexes. Therefore, the synthesis of polyamides using metal-metal bonded "diamines" and diacyl chlorides would simply lead to metal-metal bond cleavage rather than polymerization. Likewise, metal-metal bonded complexes are incompatible with many Lewis bases because the Lewis bases cleave the metal-metal bonds in disproportionation reactions.[40] This type of reactivity thus rules out many standard condensation polymerization reactions in which bases are used to neutralize any acids produced. Similar reasons prevent the use of acylchlorides in the synthesis of polyamides. All of the polymerization strategies are thus carefully designed to avoid cleaving the metal-metal bond during the polymerization process.



Scheme 2. Synthesis of an organometallic diol used in the polymer syntheses

A sample polymerization reaction, showing the synthesis of a polyurethane, was shown in Equation 3. Using similar synthetic strategies, various polyurethanes, polyureas (e.g., Equation 4), polyvinyls (e.g., Equation 5), and polyamides (e.g., Equation 6) were synthesized.[21-24] Note that the step polymers in the various equations have a metal-metal bond in every repeat unit. Experiments showed that it was not necessary to have a metal-metal bond in every repeat unit in order to photochemically degrade the polymers.[23] Copolymers are straightforwardly synthesized by adding appropriate difunctional organic molecules into the reaction mixture.

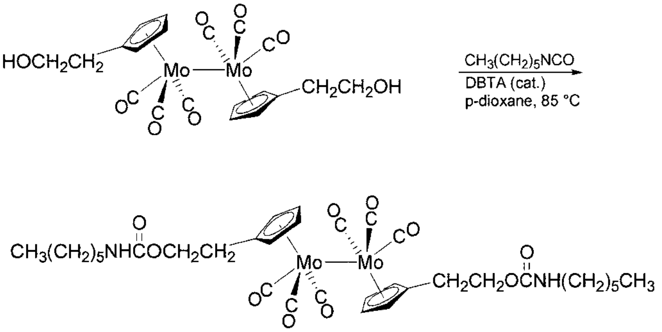
Another polymer synthesis strategy is to react the difunctional dimer molecules with prepolymers. Equation 3 shows an example of this technique.[23] (In this instance, the prepolymer is one of the Hypol polymers sold by W.R. Grace. Analysis of the sample showed it to contain, on average, three tolyl isocyanate end groups; M_n was about 2 000.)



(3)

Characterization of the Polymers.

The polymers were spectroscopically characterized by comparison of their infrared, electronic, and NMR spectra to model complexes.[21-24] For example, the product shown in Equation 8, a model complex for the polymer in Equation 3, was synthesized by reaction of $(CpCH_2CH_2OH)_2Mo_2(CO)_6$ with a *mono*isocyanate (Equation 4).



(4)

Typical M_n values, as measured by VPO or GPC, are between 5 000 and 20 000 (n = 7-25). Thus, in many cases, the polymers are best described as oligomers. However, it is important to note that no effort was made to maximize the molecular weights.

Photochemical Reactions in Solution

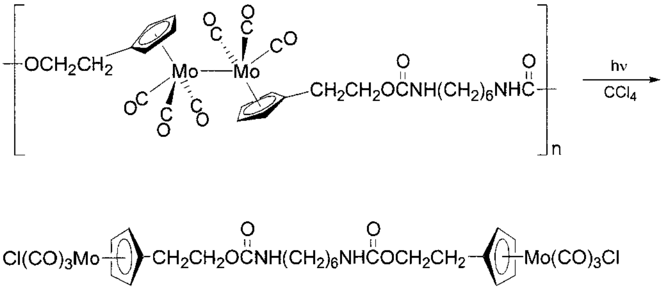
Irradiation of metal-metal bonded complexes into their lowest energy absorption band (≈ 500 nm) generally leads to one of three fundamental types of reactivity:[21, 41, 42] (1) The metal radicals produced by photolysis react with radical traps to form monomeric complexes (e.g., Equation 5). (2) The complexes react photochemically with ligands to form ionic disproportionation products (e.g., Equation 6). (3) The complexes react with oxygen to form metal oxides (Eqaution 7). (The latter reaction is likely a radical trapping reaction but may involve excited state electron transfer.) Higher energy excitation leads to M-CO bond dissociation. This type of reactivity is discussed below.

$$Cp_2Mo_2(CO)_6 + 2\,CCl_4 \xrightarrow{h\nu} 2\,CpMo(CO)_3Cl + 2\,[\bullet CCl_3] \tag{5}$$

$$Cp_2Mo_2(CO)_6 + 2\,PR_3 \xrightarrow{h\nu} CpMo(CO)_3^- + CpMo(CO)_2(PR_3)_2^+ + CO \tag{6}$$

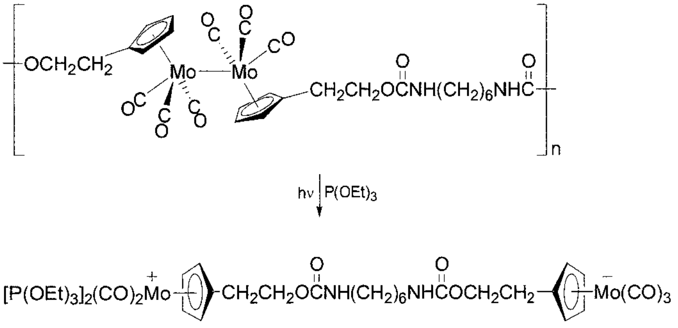
$$Cp_2Mo_2(CO)_6 \xrightarrow[O_2]{h\nu} \text{Mo oxides} \tag{7}$$

The qualitative photochemistry of the polymers in solution is analogous to the reactions of the discrete metal-metal bonded dimers in solution. [21-24] As in the photochemical reactions of the discrete dimers, the photochemical reactions of the polymers can be conveniently monitored by electronic absorption spectroscopy. The quantum yields for the reactions are in the range ≈ 0.1 to 0.6, depending on the specific polymer and the M-M bond.[22] Sample reactions of the polymers showing the three types of reactivity are shown in Equation 8-10.



(8)

A fourth type of dimer reactivity is dissociation of a CO ligand from the dimer. Generally, this type of reactivity increases in efficiency relative to M-M photolysis as the radiation energy increases.[41] In solution, this type of reactivity generally leads to substitution. However, in the case of the $Cp_2Mo_2(CO)_6$ molecule, the reaction in Equation 11 occurs.[22] (Among the dimers, this reaction to form a triply bonded product is unique to the Mo and W species.)



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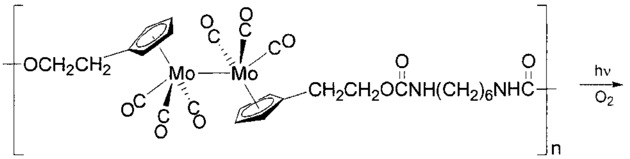

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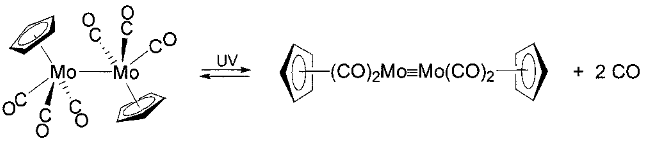
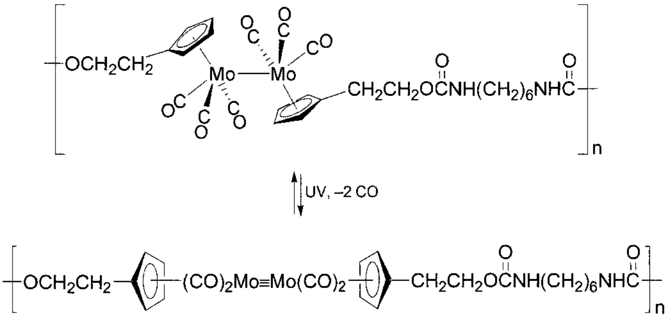


(11)

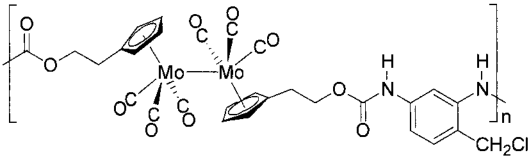
An analogous photoreaction occurs with polymers containing the Mo-Mo unit (Equation 12).



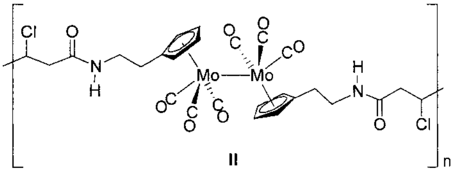
(12)

In both reactions 11 and 12, addition of CO to the product solution causes the system to back-react to reform the starting materials. Once again, the main point to be made is that the solution photochemistry of the polymers is analogous to the solution photochemistry of the discrete metal-metal bonded dimers.

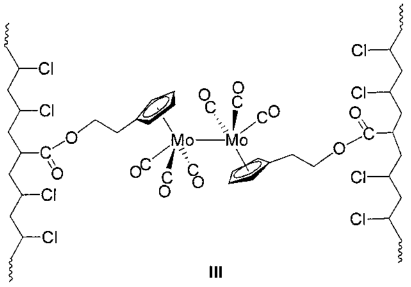
Photochemical reactivity in the absence of exogenous radical traps is possible in the case of polymers that have carbon-halogen bonds along their backbones. For example, irradiation of polymers I – III in solution in the absence of CCl_4 or O_2 led to net metal-metal bond cleavage.[43] Spectroscopic monitoring of the reaction showed that metal-metal bond cleavage is accompanied by an increase in the concentration of $CpMo(CO)_3Cl$ units. Photochemical reactions analogous to that in Scheme 3 were proposed.



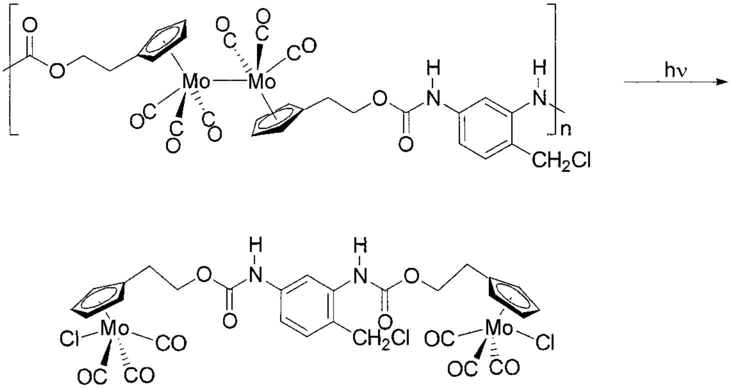
I



II



III



Scheme 3. Photochemical reaction of polymer III in the absence of an external trapping reagent

Photochemistry in the Solid State

Thin films of the polymers (≈ 0.05 mm in thickness) containing metal-metal bonds along their backbones reacted when they were exposed to visible light, whether from the overhead fluorescent lights in the laboratory, from sunlight, or from the filtered output of a high pressure Hg arc lamp. [21-24] All of the films were irradiated both in the presence and absence of oxygen. For each film and its dark reaction control, the absorbance of the $d\pi \rightarrow \sigma^*$ transition near 500 nm was monitored periodically over a period of several months. Only the polymer films that was exposed to sunlight in air completely degraded, while thin films stored in the dark in air or irradiated under nitrogen showed only slight degradation over a one-year period. From these results, it was concluded that the decomposition of the polymers requires both light and air (oxygen). Infrared spectra of the decomposition products showed the absence of products with CO ligands, as indicated by the absence of any stretches in the region 1 600-2 200 cm^{-1}. As mentioned previously, oxide complexes form in the solution phase reactions of $Cp_2Mo_2(CO)_6$ with O_2, and it was proposed that the metal-containing decomposition product of the polymer is a metal oxide.

These data suggest that oxygen is necessary for the solid-state photochemical reaction to occur. It was proposed that oxygen traps the metal radicals produced in the photolysis of the metal-metal bonds, thereby preventing radical recombination (Equation 13). If oxygen diffusion is rate-limiting then the relative rates of oligomer photochemical decomposition in the solid-state would reflect the oxygen diffusion rate.

$$\sim\sim\sim\mathrm{Mo{-}Mo}\sim\sim\sim \overset{h\nu}{\rightleftharpoons} \sim\sim\sim\mathrm{Mo}\bullet\ \bullet\mathrm{Mo}\sim\sim\sim \xrightarrow{O_2} \sim\sim\sim\mathrm{MoO_n}\quad \mathrm{O_nMo}\sim\sim\sim \qquad (13)$$

As described in the previous section, polymers I - III were designed to degrade in the absence of exogenous radical traps by building-in carbon-chlorine bonds along their backbones. As indicated, all of these polymers did degrade in the absence of oxygen when dissolved in solution. Likewise, all three polymers degraded in the solid state when irradiated in the absence of oxygen.[43]

Theories of Stress-dependent Photodegradation.

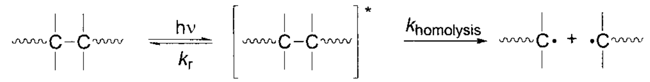
Mechanistic hypotheses to explain stress-accelerated photodegradation fall into three main categories. These categories are illustrated by reference to Scheme 4.

Scheme 4. A generalized reaction scheme showing photolysis of a bond along the backbone in a polymer (M represents a generic atom, carbon or otherwise)

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 $\phi_{\text{homolysis}}$ 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., $k_{\text{recombination}}$ is proposed to depend on stress. And last, the third category attributes the effects of stress to changes in the rate of the radical trapping reaction. The salient points of these hypotheses are outlined in the following sections.

Stress-induced Changes in $\phi_{homolysis}$.[44]

For a direct photochemical bond cleavage, the photochemical step in Scheme 4 labeled "$\phi_{\text{homolysis}}$" can be broken down into the nominal set of elementary steps shown in Equation 14. (The asterisk in Equation 14 is used to indicate an excited state of the molecule.)



(14)

Equation 14 shows the value of $\phi_{\text{homolysis}}$ (in Scheme 4) in terms of the rate constants in Equation 15. Clearly, if stress affects either k_r or $k_{\text{homolysis}}$ then $\phi_{\text{homolysis}}$ will vary with stress.

$$\phi_{\text{homolysis}} = \frac{k_{\text{homolysis}}}{k_{\text{homolysis}} + k_r} \tag{15}$$

No studies have investigated the effect of stress on k_r, but Plotnikov derived a theory for the stress dependence of $k_{\text{homolysis}}$.[44] His quantitative hypothesis attributes the increase in degradation rates with applied stress to a decrease in the activation barrier for bond dissociation in the excited state. The decrease in the activation barrier is shown pictorially in the energy state diagrams in Figure 1, which compare an unstressed bond to a stressed bond for the case of an adiabatic photochemical reaction.[45]

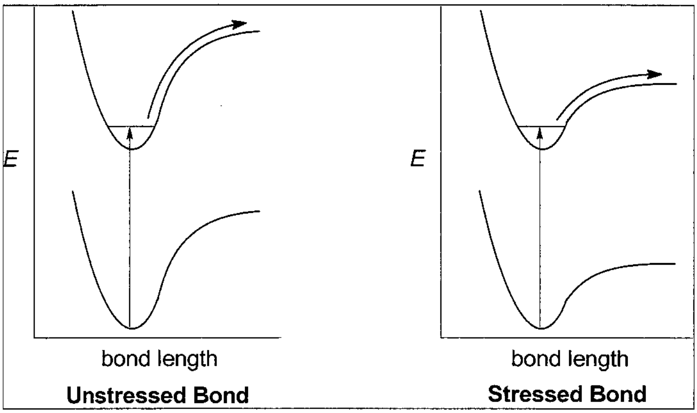


Figure 1. The photophysical origin of the Plotnikov hypothesis

Analysis of these energy surfaces led to the following equation:[44]

$$k_{\text{homolysis}} = k_0 \exp(-E_a/T) \qquad \text{where } E_a = D\left[(1-\kappa)^{1/2} - \frac{\kappa}{2}\ln\frac{1+(1-\kappa)^{1/2}}{1-(1-\kappa)^{1/2}}\right] \tag{16}$$

and where $\kappa = f/F_m$, f is the stretching force on the bond, $F_m = \alpha D^*/2$, $\alpha = \omega[\mu/2D]^{1/2}$, μ is the reduced mass, ω is the bond vibration frequency, and D and D* are the bond dissociation energies in the ground and excited states, respectively. Similar equations were also derived for the case of predissociative- and nonadiabatic-mechanisms. For each type of photochemical reaction, the theory predicts that an increase in stress will increase the quantum yield of degradation but will eventually level off, i.e., further increases in stress will not increase the quantum yield (Figure 2). The Plotnikov hypothesis has not been tested experimentally.

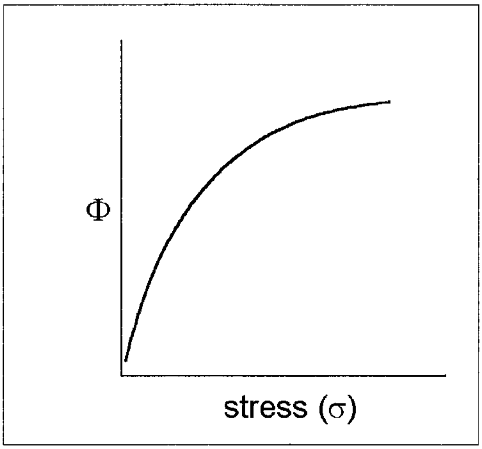


Figure 2. A plot of quantum yield for degradation vs. stress according to the Plotnikov equation

Stress-induced Changes in $k_{recombination}$

A number of authors[10, 11, 46-48] have proposed theories for explaining the stress dependence of polymer photochemical degradation rates that are based on the concept of stress affecting the ability of geminate radical pairs, formed in bond cleavage reactions, to recombine. These various theories differ slightly in their details, but they are similar overall and are discussed together here. For convenience in referring to these theories, the general concept is given the name "decreased radical recombination efficiency" (DRRE) hypothesis.

In the DRRE hypothesis, the effect of stress on the photochemical reactions of polymers is divided into four stages (Figure 3). Stage one is the low stress domain. In this stage, there is little or only slight deformation of the original polymer structure and the rate of photodegradation is not greatly affected (Figure 3).

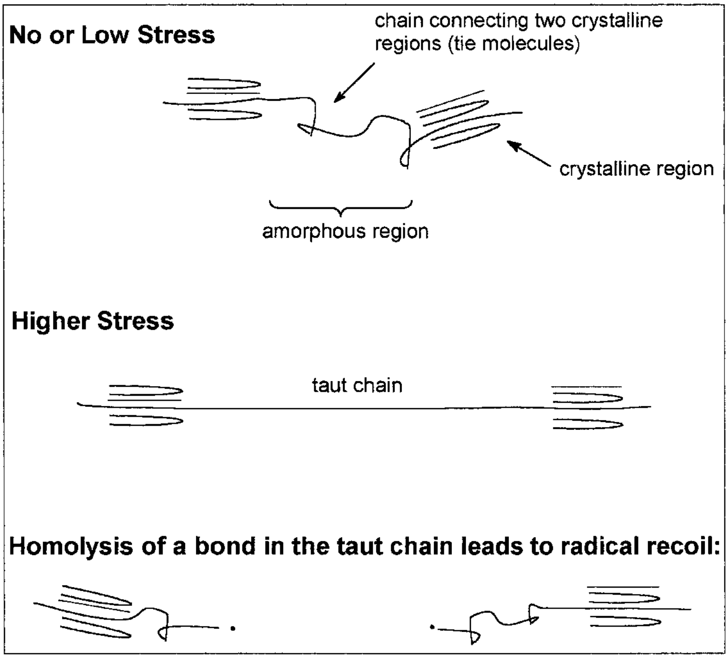


Figure 3. The proposed effect of stress in the several stages of the "decreased radical recombination" hypothesis

In stage two, higher stress causes significant morphological changes, including the straightening of the polymer chains in the amorphous regions. These straightened chains contain taut tie molecules. (Tie molecules are the interlamellar- or intercrystal-fibrils.) When bonds in the taut tie molecules are cleaved by light, the probability of radical recombination is decreased relative to non-stressed samples because entropic relaxation of the chain drives the radicals apart and prevents their efficient recombination because of their increased separation. At slightly higher stresses (stage 3), the chains are not only straightened but "stretched," and mechanical recoil also aids in the separation of the radicals (much like the mid-points of a stretched spring would fly apart if it were cut in the middle). According to this model, the role of stress is to increase the separation of the radical fragments produced by photolysis. An increased separation leads to slower radical-radical recombination, which increases the probability of radical trapping and thus of degradation.

Finally, in stage four (not shown in Figure 3), a strong stress is present, which gives the polymer a fibrillar structure with a higher degree of orientation and crystallinity. (In this stage, ordered regions develop as segments of different chains align.) Diffusion in a crystalline structure is retarded relative to the amorphous material, and the efficiency of degradation is expected to decrease because of decreased diffusion apart of the radical pair and decreased radical-trap mobility. In summary, the DRRE theory predicts that tensile stress will initially increase the quantum yield of degradation and then further increases in stress will decrease the quantum yield (Figure 4).

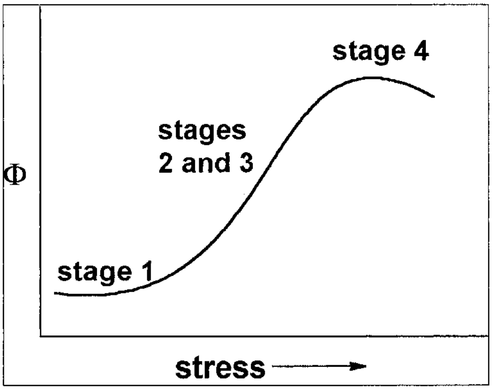


Figure 4. A plot of quantum yield for degradation vs. stress according to the decreased radical recombination hypothesis

A note of caution when interpreting data is that, if one experimentally observes a decrease in the quantum yield as predicted for stage four behavior, it is important to establish that the origin of the decrease is in fact a higher degree of orientation and crystallinity. An alternative explanation is that microcracks and fissures have formed in the sample and these are acting to relieve the stress, which in turn would also decrease the quantum yields. Nguyen and Rogers detected this alternative mechanism in their study of acrylic-melamine coatings.[49]

Stress-induced Changes in the Rates of Radical Reactions Subsequent to Radical Formation - the Zhurkov Equation

The effect of stress on reaction rates that occur subsequent to the formation of the radical caged pair is generally summarized by noting the Zhurkov equation. This empirical equation is based on Zhurkov's observation that the rates of thermal degradations show an exponential dependence on the stress.

$$\text{rate} = A \exp[-(\Delta G - B\sigma)/RT] \tag{17}$$

In this equation, ΔG is an "apparent" activation energy, σ is the stress, and A and B are constants. This equation is empirical but it has been found to describe the behavior of many thermal degradation reactions. Because the Zhurkov equation is similar in form to the Arrhenius equation,[50] this gave credence to the suggestion that stress alters the (effective) activation energy of the degradation reactions. (Recall that the Arrhenius equation shows the relationship between the activation energy for an elementary step and the rate constant for that elementary step.) The Zhurkov equation (for thermal reactions) does not specifically fit into any of the previous three categories because it deals with an "effective" activation energy, which is a composite of the activation barriers for the $\phi_{\text{homolysis}}$, $k_{\text{recombination}}$, and k_{trapping} steps.

The suggestion has been made that a Zhurkov-like equation might also apply to photochemical degradation reactions.[1] A version of the equation suitably modified for a photochemical reaction has never appeared explicitly in the literature, but the following general equation is implied:

$$\Phi_{\text{obs}} = A \exp[-(\Delta G - B\sigma)/RT] \tag{18}$$

(Several authors note that the photochemical equation should contain the light intensity as a variable.[1] In the equation above, the intensity dependence of the *rate* is found in the quantum yield, which recall is the rate divided by the intensity. Additional intensity dependences might show up in the A and B terms.) A plot of quantum yield as a function of stress for a system that follows Zhurkovian behavior is shown in Figure 5.

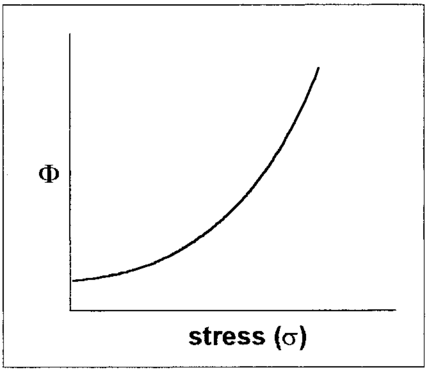


Figure 5. A plot of quantum yield for degradation vs. stress according to the Zhurkov equation

Experimental Studies of Stress on Photochemical Degradation Efficiencies

Thin films of polymer **III** were photochemically reactive ($\lambda > 500$ nm) in the absence of oxygen.[43] A Cl-atom abstraction reaction analogous to the reaction in Scheme 3 was proposed because infrared spectroscopic monitoring of the photochemical reaction showed the disappearance of the $\nu(C\equiv O)$ bands of the $Cp_2Mo_2(CO)_6$ moiety at 2 009, 1 952, and 1 913 cm^{-1} and the appearance of bands attributed to the $CpMo(CO)_3Cl$ unit at 1967 and 2047 cm^{-1}. The application of tensile stress changed the photodegradation efficiency, and a plot of relative quantum yield vs. stress is shown in Figure 6. Note that tensile stress initially caused the quantum yield to increase, but after a certain point additional stress caused a decrease in the quantum yield.

These results are consistent with the “decreased radical recombination” (DRE) hypothesis. All three hypotheses discussed in the previous section predict that stress will initially increase the efficiency of degradation, but only the “decreased radical recombination” hypothesis predicts that further increases in stress will eventually cause a decrease in photochemical efficiency. The conclusion, at least in this one system, is that the role of stress is to increase the separation of the photochemically generated radical pair, which decreases their probability of recombination. To the authors, knowledge, this is the first and only experimental confirmation of the behavior predicted by the "decreased radical recombination" hypothesis in which oxygen diffusion is not a complicating factor. (Note that x-ray scattering and infrared spectroscopy experimentally confirmed the increase in chain order in the stressed PVC polymer used in these experiments.)

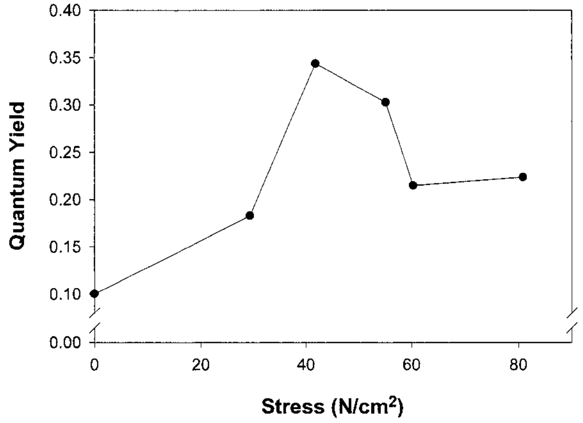


Figure 6. Quantum yields for degradation of **III** vs. applied tensile stress

Further evidence for the role of the DRRE mechanism in determining how stress affects degradation rates comes from the effect of plasticizer on a polymer. Because plasticizers increase chain-end mobility, one would predict that a plasticized polymer should have a higher quantum yield for degradation, at any given stress, compared to the unplasticized polymer at the same stress. Likewise, because chain alignment should be facilitated, the maximum in the curve of Φ vs. stress should occur at a lower stress. To test these predictions and to further test the DRRE hypothesis on which they are based, the plasticizer DOP was added to polymer II (25% plasticizer) and the effect of stress on Φ was measured. (The new material had a glass transition temperature of less than 25 °C.) As predicted, the quantum yields at any particular stress were higher for the plasticized material and the maximum in the curve occurred at lower stress.[51] Both results are consistent with the DRRE hypothesis.

Summary

Step polymers containing metal-metal bonds along their backbones can be synthesized by reacting difunctional, cyclopentadienyl-substituted metal carbonyl dimers with appropriate difunctional organic molecules. A synthesis of a polyurethane was shown, but a wide variety of polymers, including polyureas and polyamides, have been synthesized by analogous routes using appropriate starting materials. Although not discussed, it is noteworthy that chain polymers containing metal-metal bonds can be synthesized from metal-metal dimers containing Cp ligands with vinyl group substituents. The polymers are photodegradable because the metal-metal bonds homolyze when irradiated with visible light. The photochemical reactions of the polymers in solution are identical to the photochemical reactions of the discrete metal-metal bonded dimers. Typical reactions include metal-metal bond disproportionation and chlorine atom abstraction from carbon tetrachloride. The polymers are also photochemically degradable in the solid state; thin films of the polymers degrade when irradiated with visible light in the presence of oxygen or if the polymer backbone has a built-in radical trap. Tensile stress increases the rate of polymer photodegradation. The interpretation of the plots of quantum yield for degradation vs. stress is that the role of stress is to increase the separation of the radical fragments produced by photolysis. An increased separation leads to less radical-radical recombination, which increases the efficiency of degradation. Quantitative knowledge of these and other factors that control polymer degradation rates will eventually allow synthesis of an ideal photodegradable polymer - one that has a tunable onset of degradation and that degrades quickly once degradation has started.

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