Investigation of the Origin of Tensile Stress-Induced Rate Enhancements in the Photochemical Degradation of Polymers

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An interesting outcome of artificial weathering studies on polymers is the discovery that tensile and shear stress can accelerate the rate of photodegradation.[1,2] This phenomenon is general and has been observed with many polyolefins, including polystyrene,[3] polypropylene,[4] polyethylene,[5] polyethylene/polypropylene copolymer,[6] PMMA,[7] and polyfluorocarbons,[8] as well as with polycarbonates,[4e] nylons,[9] acrylic-melamine coatings,[10] and various elastomers and rubbers.[11,12] The occurrence of stress-accelerated photodecomposition is a phenomenon 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.[13] The fundamental question, as yet unanswered, is: why does stress cause changes in the photodegradation rates of polymers? Attempts to answer this question have generally been hampered by the mechanistic complexity of the degradation reactions.[1d] 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 oxygen diffusion is the rate-limiting step in many photooxidative degradations.[5d,14] This adds to the intricacy of the analysis because oxygen diffusion rates are frequently time-dependent.[14,15]

To circumvent these experimental and mechanistic complexities, we designed a variety of new photochemically degradable polymers that contain metal−metal bonds along the backbone.[16−21] When exposed to visible light, these polymers degrade by a straightforward mechanism involving metal−metal bond homolysis followed by capture of the metal radicals with a metal−radical trap (typically either oxygen or an organic halide; Scheme 1). To eliminate the

**Scheme 1.** Photochemical Reaction of the Polymers That Have Metal−Metal Bonds along Their Backbones
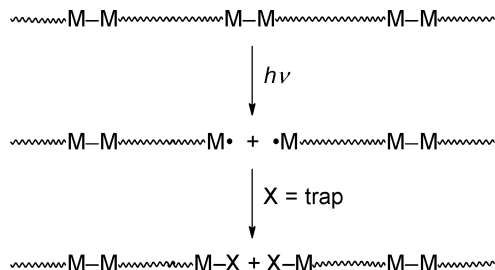
kinetically complicating effects of rate-limiting oxygen diffusion, we incorporated built-in metal−radical traps along the polymer backbones (i.e., the trap X in Scheme 1 is attached to the polymer backbone). In this Communication, we report the results of our study on the effects of stress on the photochemical degradation efficiencies of the modified PVC polymer **1**. The results allowed us to pinpoint the chemical origin of the stress-induced acceleration of the photochemical degradation of **1**.

1
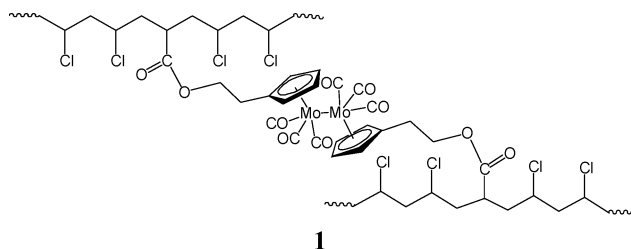
$Cp(CO)_3Mo−Mo(CO)_3Cp$ ($Cp = \eta^5\text{-}C_5H_5$) chromophores were introduced into the backbones of PVC using the synthetic scheme shown in Scheme S1 (Supporting Information). Thin films of **1** were photochemically reactive ($\lambda > 500$ nm) in the absence of oxygen. Infrared spectroscopic monitoring of the photochemical reaction showed the disappearance of the $\nu(C{\equiv}O)$ bands of the $Cp_2Mo_2(CO)_6$ moiety at 2009, 1952, and 1913 cm^{-1} and the appearance of bands attributed to the $CpMo(CO)_3Cl$ unit at 1967 and 2048 cm^{-1}.[16−21] (The reaction is shown schematically in Scheme S2.) The application of tensile stress changed the photodegradation efficiency, and a plot of relative quantum yield versus stress is shown in Figure 1. 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.

Three hypotheses that attempt to explain the relationship of stress to photodegradation efficiencies have been proposed in the polymer literature. (All three hypotheses make the assumption that radical trap diffusion is not the rate-limiting step.) (1) The Plotnikov hypothesis[22] attributes the increase in degradation rates with applied stress to a decrease in the activation barrier for bond dissociation in the excited state. (2) The "decreased radical recombination efficiency" hypothesis of Busfield,[5b] Rogers,[5c,23] Baimuratov,[24] and others[25] proposes that, at low to moderate stresses, radical−radical recombination of bonds cleaved along the polymer backbone is less efficient, which leads to an increase in degradation efficiency. (See Figure S1 for a pictorial explanation.) As the stress increases, however, segments of different chains align, which induces a higher degree of orientation and crystallinity in the polymer, which in turn makes diffusion more difficult. The efficiency of degradation is predicted to decrease accordingly because of decreased radical (and/or trap) mobility in the ordered polymer. (3) The final hypothesis is the photochemical analogue of the Zhurkov equation used to analyze the effect of stress on thermal degradations. This equation, which relates degradation rates to stress, is essentially a stress-modified Arrhenius equation.[26]

All three hypotheses predict that stress will initially increase the efficiency of degradation, but only the "decreased radical recombination efficiency" hypothesis predicts that further increases in stress will eventually cause a decrease in photochemical efficiency, as was found in this study.[27] The results of this study are therefore consistent with the "decreased radical recombination efficiency" hypothesis, from which it can be concluded that the role of stress
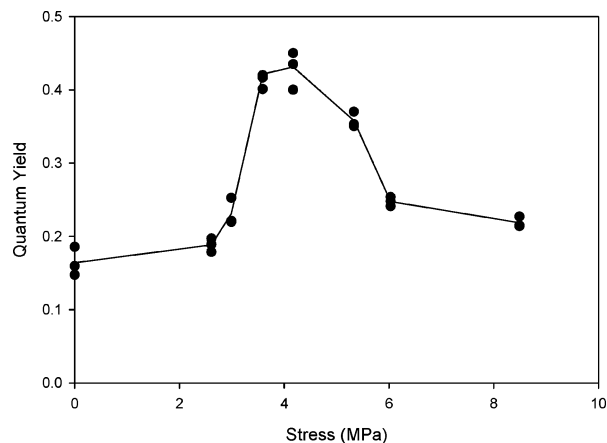
Figure 1. Quantum yields for degradation of **1** versus applied tensile stress. The results of three independent measurements at each stress are shown.

is to increase the separation of the photochemically generated radical pair, which decreases their probability of recombination. To our knowledge, this is the first experimental confirmation of the behavior predicted by the "decreased radical recombination efficiency" hypothesis in which oxygen diffusion is not a complicating factor.

X-ray diffraction and IR spectroscopy are both commonly used to assess crystallinity in PVC,[28−35] and both techniques clearly showed that stress increased the chain ordering in polymer **1**. In the case of IR spectroscopy, an increase in the absorbance ratio of the infrared peak at 635−638 to that at 610−615 cm^{-1} is indicative of an increase in crystallinity.[28−32] Figure S2 shows that the A_{637}/A_{615} ratio of polymer **1** increased with increasing stress. In the case of wide-angle X-ray diffraction, an increase in intensity of the (200) and (110) reflections (in the 16−18° 2θ region[33−35]) has been shown to correlate with an increase in crystallinity in PVC. Figure S3 shows that these peaks grew in and increased in intensity with increasing stress, again consistent with the conclusion that stress is increasing the chain ordering in polymer **1**.

Unlike the Plotnikov and Zhurkov hypotheses, there is no equation in the "decreased radical recombination efficiency" hypothesis that quantitatively relates quantum yields to stress. Efforts are underway in our lab to determine such a quantitative relationship.

Supporting Information Available: Experimental details describing the synthesis and irradiation of polymer **1**; plots of infrared and X-ray data showing the increase in order with increasing stress (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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