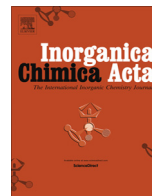




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Review

Metal–metal bond photochemistry as a tool for understanding the photochemical degradation of plastics



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ABSTRACT

Research from the author's laboratory is reviewed on the photochemistry of polymers that have metal–metal bonds incorporated into their backbones. These polymers are useful for studying the mechanistic aspects of polymer photodegradation because irradiation with visible light causes photolysis of the metal–metal bonds with subsequent degradation of the polymer backbone. The relative simplicity of the degradation process in these polymers facilitates detailed mechanistic studies. In contrast, the degradation pathways in “regular” polymers are intricate, and consequently it is difficult to do detailed mechanistic studies of photodegradation. Two mechanistic studies involving the metal–metal-bond-containing polymers are reviewed. The first study investigated why the kinetics of photochemical degradation are biphasic. Using the polymers with metal–metal bonds, it was shown that the biphasic kinetics arise because the photochemically generated radicals are initially formed in one of two environments. In one environment, a radical trap is within the immediate reactive sphere of the radical; in the other environment, no radical trap is present. The second study examined the temperature dependence of the photochemical degradation reactions in the polymers. The temperature dependence was shown to arise from secondary chain movements of the polymers. It is emphasized that similar studies using regular polymers would have been more difficult to carry out and interpret.

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David R. Tyler received Bachelor of Science degrees in chemistry and mathematics from Purdue University in 1975. While an undergraduate at Purdue, he did research with Professor R. A. Walton on the reactivity of the $Re_2X_8^{2-}$ anions and on the X-ray photoelectron spectra of transition metal chloride complexes. He received his Ph.D. degree in June 1979, from the California Institute of Technology where he worked with Professor Harry B. Gray on the photochemistry and electronic structures of metal carbonyl cluster complexes. In the early part of his career, Tyler's interests were in the area of metal radical chemistry, during which time he developed the chemistry of 19-electron adducts. Although such molecules were initially met with considerable skepticism because they were theoretically predicted to not exist, Tyler's students developed ingenious mechanistic experiments to show their existence, and they went on to demonstrate that these molecules were important intermediates in numerous radical reactions. Tyler's current research interests are in photochemically degradable plastics; the development of new homogeneous catalysis for use in aqueous solution; and photochemistry, particularly the investigation of reactions on the femtosecond timescale. He has absolutely no interest in administration, having served as department head from 1995 to 1998. Tyler is the author of over 230 research publications.

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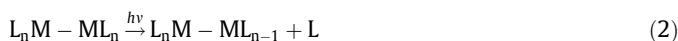
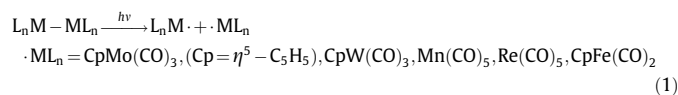
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1. Introduction

The photochemistry of complexes with metal–metal bonds has been investigated for nearly five decades [1–3]. Complexes with metal–metal bond orders from 1 to 4 have been studied [4–6], but most work has focused on the photochemistry of complexes with single metal–metal bonds [7]. For these complexes, two primary photochemical reactions are common: metal–metal bond homolysis (Eq. (1)) and metal–ligand (typically M–CO [8]) bond dissociation (Eq. (2)). In the case of organometallic complexes, metal–metal bond cleavage predominates at low-energy irradiation wavelengths, and the metal–ligand bond dissociation process generally increases in efficiency as the energy of the exciting radiation increases. Both the mechanistic aspects and the synthetic applications of these photochemical reactions have been probed in detail, and numerous literature reports have extensively reviewed these studies [7,9–16].



Research in our laboratory has focused on an applied aspect of metal–metal bond photochemistry: we use the metal–metal bond photolysis reaction as a way to probe the photochemical degradation of polymers. In particular, we use the metal–metal photolysis reaction to study the mechanistic aspects of polymer photodegradation that would otherwise be nearly impossible to investigate. This paper reviews two studies from our laboratory in which metal–metal bond photochemistry was critical for understanding polymer photodegradation. Before reviewing these topics, however, a brief overview of photochemically degradable plastics is presented and an explanation of why metal–metal bonded complexes are good models for polymer degradation is discussed.

2. Photochemically degradable plastics

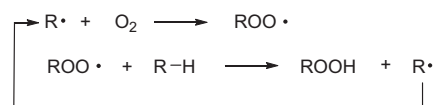
2.1. The compelling need for degradable plastics

There are compelling economic and social reasons for using degradable plastics in selected applications [17]. The primary application for degradable plastics is in agriculture, specifically in a farming method called plasticulture [18–21]. In this method,

fields are covered with plastic sheeting, which acts as a mulch to inhibit weed growth, keep moisture in, and keep the ground warmer. If photodegradable plastics are used, getting rid of the plastic at the end of the growing season is not an issue. A second, emerging application for degradable plastics is for environmental purposes [22]. The build-up of plastic litter in the environment is a concern, and plastics that degrade after use is one approach to alleviating this problem. Because of these important applications, considerable research is devoted to devising and studying photodegradable plastics [23–27].

There are two basic methods for making polymer materials photochemically degradable [23,24]. One method is to incorporate a reactive chromophore into the polymer chains. The most commercially successful chromophore is the carbonyl group [23,24,28]. Absorption of UV radiation by such polymers leads to backbone degradation by Norrish Type I and II processes and by the standard radical autooxidation cycle (Scheme 1). The second general method for making polymer materials photochemically degradable is to mix in a radical initiator during the compounding of the plastic [17,23,29]. Light or thermal activation of the initiator forms radicals; once radicals have formed in a polymer sample, the chains degrade by the autooxidation cycle.

Although it is understood how to make polymers photodegradable, the long-term goals are to control the onset of degradation (specifically, until after the plastic's useful lifetime) and the rate of degradation. These aspects of the degradation process are, as of yet, not controllable. In order to design a polymer that will photochemically degrade after its useful lifetime and to control its rate of degradation, it is necessary to identify the environmental and molecular (structural) parameters that affect polymer degradation rates and to understand in a mechanistic sense how these parameters affect the degradation [30]. Unfortunately, several challenging experimental problems hinder the rigorous mechanistic exploration of polymer photodegradation. The chief problem is that the degradations are mechanistically



Scheme 1. The propagation steps in a radical autooxidation cycle. The hydroperoxides (ROOH) that form in this process have subsequent chemistry that generates more radicals and accelerates the degradation process.

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