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Applications of the Tachiya Fluorescence Quenching Model To Describe the Kinetics of Solid-State Polymer Photodegradation

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INTRODUCTION

One strategy for reducing the persistence of plastics in the environment is to use plastics that photochemically degrade after use.[1−4] Mechanistic knowledge of polymer degradation reactions is essential for designing such plastics. Many mechanistic studies of polymer photodegradation include a kinetics investigation, and the interpretation of the kinetics data can reveal important insights about the environmental and molecular parameters that affect the onset of polymer degradation and the degradation rates.[5,6] Several challenging experimental problems hinder the rigorous experimental mechanistic exploration of polymer photodegradation.[7] To circumvent these mechanistic complexities and therefore make it less difficult to interpret data and obtain fundamental insights, we use polymers that have metal−metal bonds incorporated into the polymer backbone.[7,8] A thorough explanation of why we use these polymers is found in our previous publications[5−11] so it is simply noted here that irradiation of these materials causes the metal−metal bonds to break and that subsequent trapping of the metal radicals with an appropriate radical trap (such as molecular oxygen or a carbon−chlorine bond) leads to net backbone cleavage (Scheme 1).[8] The degradation reactions of these polymers can be conveniently monitored spectroscopically using the metal−metal bond chromophore. The degradation kinetics typically follow a biphasic decay in which there is a short, nonlinear component and a longer-lived, slowly evolving linear component.[2,7,12] This biphasic behavior is typical for many polymer photodegradation reactions (not just the polymers containing metal−metal bonds), and it led us to propose a model to explain the biphasic kinetics behavior.[7]

Our model to describe polymer photodegradation kinetics was inspired by Perrin's model of fluorescence decay rates.[13] The Perrin model was originally proposed to explain the nonlinear fluorescence quenching of small molecules embedded in solid polymers, and it posits that the fluorescent molecules are present in one of two microenvironments (Figure 1). In one microenvironment, a fluorescence quencher is within the "quenching sphere" of the excited molecule, and this leads to quenching. In the second microenvironment, no quencher molecule is inside the quenching sphere, and no quenching will occur because diffusion into the quenching sphere is slow compared to the lifetime of the excited state.[13] The biphasic kinetics is attributed to the combination of the fast initial decay of the fluorescence due to quenchers within the quenching sphere and the slower decay that is attributed to the natural lifetime of the excited species that are in the microenvironment with no quencher.[7]

In our model of polymer photodegradation kinetics, the excited fluorescent species of the Perrin model is conceptually replaced by the photogenerated radicals, and radical traps replace the quencher molecules. Analogous to the Perrin model, the radicals can exist in one of two environments (Figure 2). In one microenvironment, a radical trap is present in the "reaction sphere" of the radical, and in the other microenvironment, no trap is present in the reaction sphere of the radical. To account for the slower (linear) part of the biphasic decay, it was proposed that diffusion of a trap into the reaction sphere during the lifetime of the radical occurred. A potential problem with this proposal is that diffusion is slow in the solid state and the lifetime of the radicals is short. For example, molybdenum radicals similar to those embedded in the polymer backbones can recombine in solution with a time constant on the order of 5 ps, as determined by ultrafast spectroscopy.[9] Consequently, diffusion of a trap into the reactive sphere of a radical may not be possible during the short lifetime of the metal radicals.

After publication of our model, Professor M. Tachiya suggested to us in a personal communication that a model involving a Poisson distribution of radical/trap environments (not just two) could account for the biphasic kinetics.[14,15] An important feature of Tachiya's suggestion is that it is not necessary to postulate that diffusion of a trap into the reaction sphere of the radical occurs during the lifetime of the radical in order to get biphasic behavior. In this Note, we discuss the application of the Tachiya model to solid-state polymer photodegradation, and we compare the Tachiya model to the Perrin-like model.

EXPERIMENTAL SECTION

Materials and Methods. The polymer materials and experimental setup used to monitor photodegradation have been described previously.[7,10] Polyurethane and poly(vinyl chloride) (PVC) polymer samples containing molybdenum−molybdenum (Mo−Mo) bonds, polymers **1** and **2** (Figure 3), were prepared according to literature procedures.[5,16] Irradiation of the polymers was carried out at 532 nm with a 200 W mercury arc lamp or a 5 mW frequency-doubled Nd:YAG laser to induce cleavage of the Mo−Mo bonds. The photodegradation process was monitored using an Oriel Merlin radiometry instrument described elsewhere.[10] The sample temperatures were regulated, and transmittance of the samples was monitored at 3 s intervals over 50 min. Several scans were taken across the sample films for reproducibility. The

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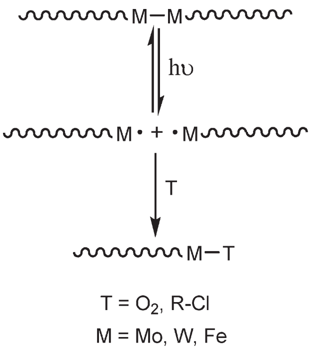
data were fit to the Perrin-like model[7] and to the Tachiya model using Igor-ProCarbon software.

RESULTS AND DISCUSSION

The decay curves for the photochemical degradation of polymers **1** and **2** showed biphasic behavior.[7] As summarized in the Introduction, our original explanation for the observed biphasic photochemical degradation kinetics was based on a Perrin-like model (Figure 2).[7] Analysis of this model led to the rate expression in eq 1, where [P] denotes the concentration of Mo—Mo bonds, k_1 and k_2 are constants, and X_0 and Y_0 represent the initial concentrations of Mo—Mo bonds in the two different microenvironments. (Note that the observed rate of polymer degradation is the sum of the rates for the radical trapping reactions in the two microenvironments.) Results of the fits of the photodegradation traces for polymers **1** and **2** to eq 1 were previously reported and they were quite good.[7]

Scheme 1. Photodegradation of a Polymer Containing Metal—Metal Bonds in Its Backbone



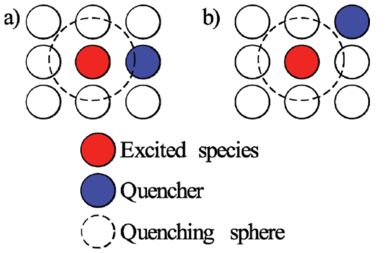


Figure 1. Physical description of the Perrin-like kinetic model (a) with the quencher in the quenching sphere and (b) with the quencher outside the quenching sphere.[7]

$$[\mathrm{P}] = X_0 - k_1 t + Y_0 \mathrm{e}^{-k_2 t} \tag{1}$$

As mentioned in the Introduction, a potential problem with the Perrin-like mechanism is that diffusion of a trap into the reactive sphere of a radical may not be possible during the short radical lifetime. To avoid this problem, yet still have biphasic degradation kinetics, we propose an alternative mechanism based on the kinetics analysis of fluorescence quenching by Tachiya.[14,15] The mechanism is outlined in eqs 2—4. Note that, in this alternative mechanism, metal—metal bonds can only react if they have a trap in their reaction sphere before photolysis.

$$\mathrm{M}_n\text{—}\mathrm{M}_m + \mathrm{T} \overset{\textit{diffusion}}{\rightleftharpoons} (\mathrm{M}_n\text{—}\mathrm{M}_m, \mathrm{T}) \tag{2}$$

$$(\mathrm{M}_n\text{—}\mathrm{M}_m, \mathrm{T}) \xrightarrow{h\nu} (\mathrm{M}_n\bullet, \bullet\mathrm{M}_m, \mathrm{T}) \tag{3}$$

$$(\mathrm{M}_n\bullet, \bullet\mathrm{M}_m, \mathrm{T}) \rightarrow \mathrm{M}_n - \mathrm{T} + \bullet\mathrm{M}_m \tag{4}$$

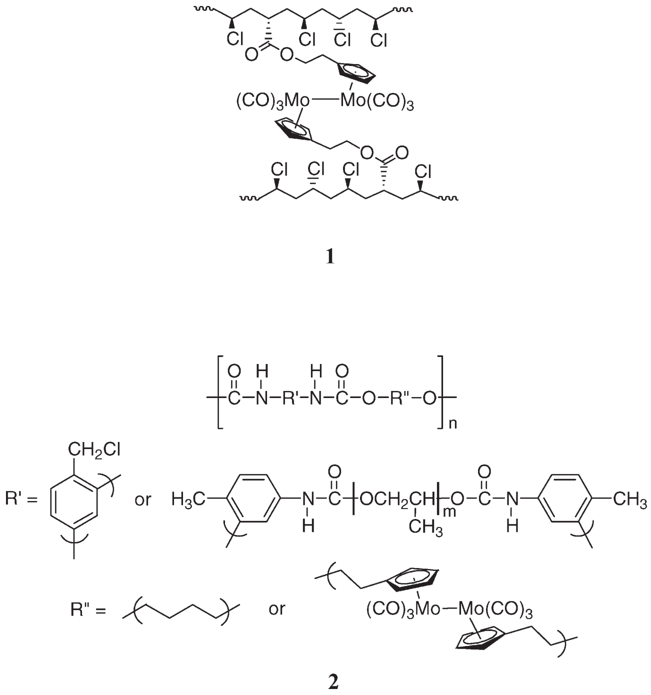


Figure 3. Photoactive polymers used for photodegradation studies. Polymer **1** is a cross-linked PVC, and polymer **2** is a polyurethane with a mixture of rigid and flexible linkages.

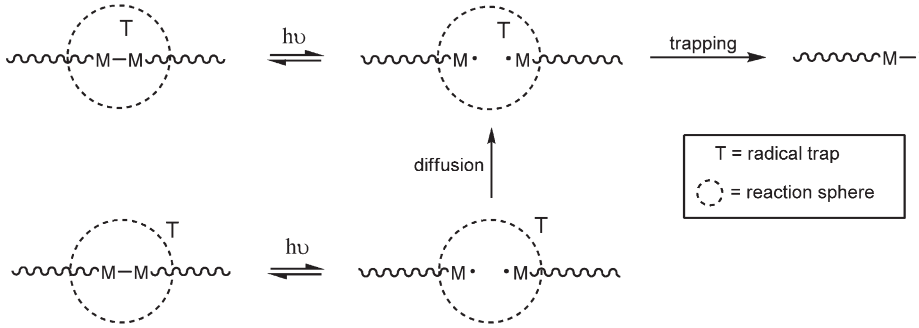


Figure 2. Mechanistic description of the photodegradation of polymers according to the Perrin-like model.

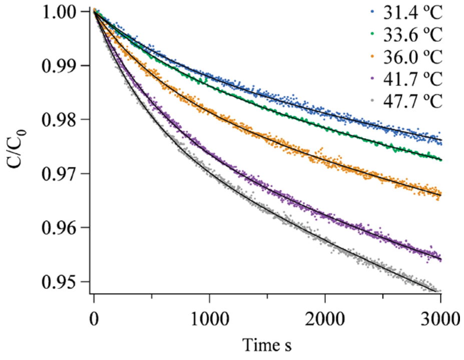


Figure 4. Relative Mo−Mo concentration as a function of irradiation time at various temperatures for polymer **1** with fits to the Tachiya model (eq 7). The temperatures for each run are denoted in the plot.

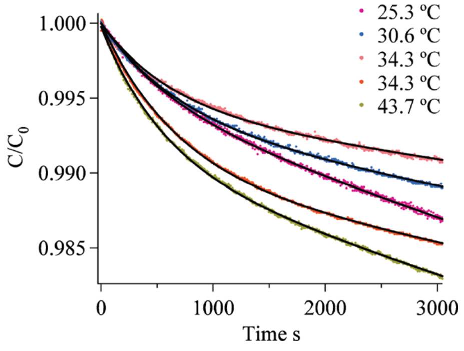


Figure 5. Relative Mo−Mo concentration as a function of irradiation time at various temperatures for polymer **2** with fits to the Tachiya model (eq 7). The temperatures for each run are denoted in the plot.

The kinetics analysis of this mechanism is analogous to a model originally developed by Tachiya to describe the luminescence quenching of excited species in micelles.[14,15] This model is shown in eqs 5 and 6. In these equations, P_n* stands for a micelle that contains an excited molecule and n quencher molecules, and T represents a quencher molecule.

$$P_n^* + T \underset{(n+1)k_-}{\overset{k_+}{\rightleftharpoons}} P_{n+1}^* \tag{5}$$

$$P_n^* + T \xrightarrow{nk_q} P_n \tag{6}$$

When applied to the mechanism in eqs 2−4, the symbol P_n^* stands for the concentration of metal−metal bonds that have n radical traps within a volume V around each metal−metal bond, and the symbol T stands for a radical trap molecule. Equation 5 describes the entry and exit of a radical trap into and out of the volume V around the metal−metal bond. Equation 6 describes the process in which the metal−metal bond is cleaved with visible light, and the resulting metal radical is captured by a radical trap. In his analysis of this mechanism, Tachiya arrived at two important conclusions. First, the distribution of the number of radical traps in the volume V around each metal−metal bond obeys a Poisson distribution. (See eq 8 of ref 15.) Second, the concentration of P* is given by the expression in eq 7, where k_q and k_- are the rate constants defined in eqs 5 and 6 and n_{bar} is the average number of radical traps in the volume V.

$$\frac{P^*(t)}{P^*(0)} = \exp\left\{-\left[\frac{k_- k_q n_{bar}}{k_- + k_q}\, t\right] - \left[\frac{k_q^{\,2} n_{bar}}{(k_- + k_q)^2}\right]\left[1 - e^{-(k_- + k_q)t}\right]\right\} \tag{7}$$

Equation 7 was used to fit the photodegradation curves of polymers **1** and **2**. The resulting fits are shown in Figures 4 and 5 for

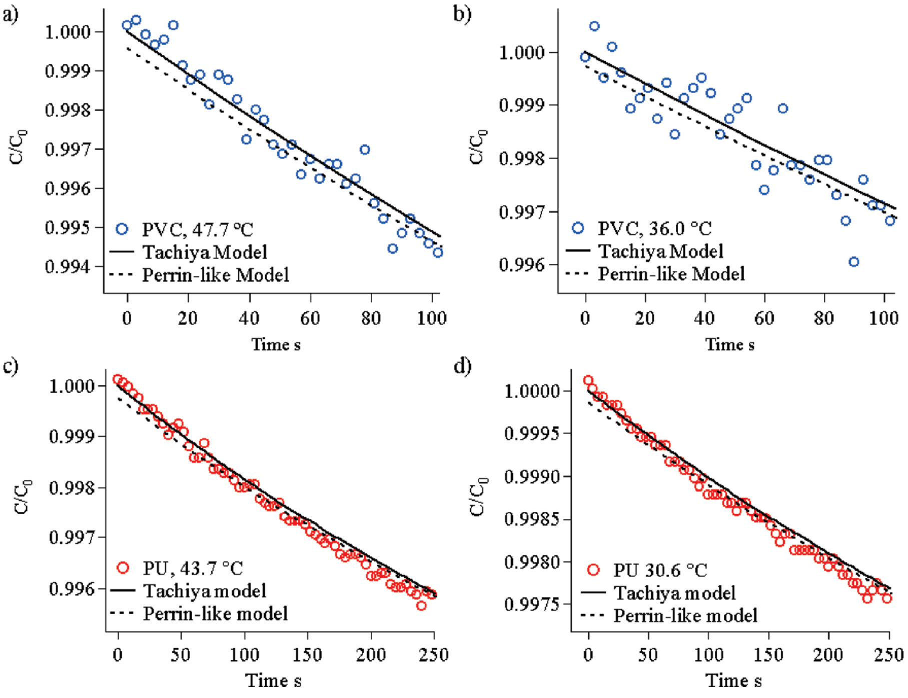


Figure 6. Example comparisons of the Tachiya and Perrin-like models at early times fit to the degradation of polymer **1** at (a) 47.7 °C and (b) 36.0 °C and polymer **2** at (c) 43.7 °C and (d) 30.6 °C.

temperatures ranging from 25 to 50 °C. It is clear from both Figures 4 and 5 that the Tachiya model fits the data extremely well. Although an excellent fit in and of itself is not evidence for a mechanism, the pathway in eqs 2−4 avoids the need to have a step involving diffusion of a trap to a short-lived radical. The Tachiya mechanism seems more likely in this regard.

Comparison of the Perrin-like and Tachiya fits provides further insights. Data for the first few minutes of several representative photodegradation reactions are plotted in Figure 6. The corresponding fits for the Tachiya and Perrin-like models are also shown. Note that the Tachiya model fits the data more closely at these short times. In contrast, the Perrin-like model slightly underestimates the population of intact metal−metal bonds at the onset of the decay curve. In other words, the Perrin-like model overestimates the amount of initial radical trapping that occurs. A very qualitative explanation of this result may be that the two-state Perrin model is less responsive than the Tachiya model, which has a continuum of trap distributions (a Poisson distribution) and is therefore able to fit the data better. (It is noted that Dorrance and Hunter showed that the distribution of quenching molecules (in our case radical traps) in kinetic models is an important parameter in describing the kinetics of systems.[17]) Although Figure 6 does show that the Perrin-like model overestimates the amount of initial photodegradation, this is true only for the first few minutes. At longer times, the Perrin-like model fits the data well.

In summary, the biphasic kinetics of a typical photochemical degradation reaction of a polymer can be interpreted using either a Perrin-like kinetics model (Figure 2) or a Tachiya-like model (eqs 2−4). The former model invokes a mechanism in which photoproduced radicals are formed in one of two microenvironments. In one microenvironment, a radical trap is present in the reaction sphere of the radical, and in the other microenvironment, no trap is present. In contrast, analysis of the Tachiya model shows a Poisson distribution of radical traps around the radical. The Tachiya model gives better fits to the experimental kinetics data at short reaction times. Although a better fit does not necessarily favor the Tachiya model, from a mechanistic viewpoint the Tachiya model would seem to be more likely because it does not require diffusion of a radical trap to the short-lived radical, a process that would be slow in the solid state in comparison to the lifetime of the radical.

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