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Photochemically Reactive Polymers. Identification of the Products Formed in the Photochemical Degradation of Polyurethanes That Contain $(C_5H_4R)(CO)_3Mo{-}Mo(CO)_3(C_5H_4R)$ Units along Their Backbones

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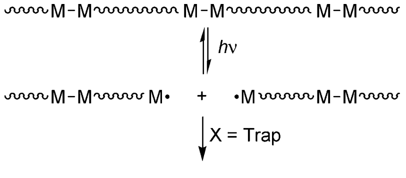
A photochemically degradable polyurethane with Mo−Mo bonds along its backbone (**I**) was synthesized by reacting the isocyanate-capped poly(ethylene glycol) prepolymer Hypol 2000 with the Mo−Mo-bond-containing diol $(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$. A copolymer (**II**) that contained poly(ethylene glycol) in addition to Hypol 2000 and $(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$ was also synthesized. The backbones of both polymers can be photochemically cleaved, because the Mo−Mo bonds homolyze when irradiated with visible light. A net photochemical reaction only occurs in the presence of a radical trap, such as oxygen in the air; no net photochemical reaction occurs in the absence of radical trap. X-ray photoelectron spectroscopy shows that the Mo oxidizes during the photochemical reaction in air, initially to Mo(V) and then to Mo(VI). Both products are likely oxide species. Infrared spectroscopy confirms the release of CO when the polymers are irradiated. A polyurethane copolymer (**III**) that photochemically degrades in the absence of oxygen was synthesized by reacting $(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$ and 1,4-butanediol with tolylene 2,4-diisocyanate terminated poly(propylene glycol) and 1-(chloromethyl)-2,4-diisocyanatobenzene. The Cl atoms are readily abstracted by the photochemically generated Mo radicals, and this polymer readily degrades when irradiated in the absence of air. Despite the relatively low concentration of Cl in this polymer, the quantum yield for photodegradation is remarkably high (0.35). Other polymers with much higher concentrations of Cl trap are less reactive, and it is concluded that T_g is an important parameter in determining the efficiency of photochemical degradation. It is proposed that because chain motion occurs above T_g, the radical trapping reaction is more facile, resulting in more net reaction.

Introduction

Photochemically reactive polymers[1−5] are of considerable interest, because they are useful as photodegradable plastics, photoresists, and biomedical materials and as precursors to ceramic materials.[6−9] With regard to photodegradable plastics, it might seem strange to intentionally design a polymer material that falls apart when exposed to light, especially in view of the enormous efforts made by polymer chemists over the years to make their materials stable to light.[1,2] However, there are compelling economic and environmental reasons for using degradable plastics in certain applications, and therefore considerable research is now devoted to devising new photodegradable polymers with improved performance. In previous papers, we described the synthesis of a new class of photodegradable polymers that have metal−metal bonds along the polymer backbone.[10−13] These polymers are photochemically active, because metal−metal bonds can be cleaved with visible light:[14]



Our syntheses of metal−metal-bond-containing polymers use metal−metal-bonded organometallic dimers

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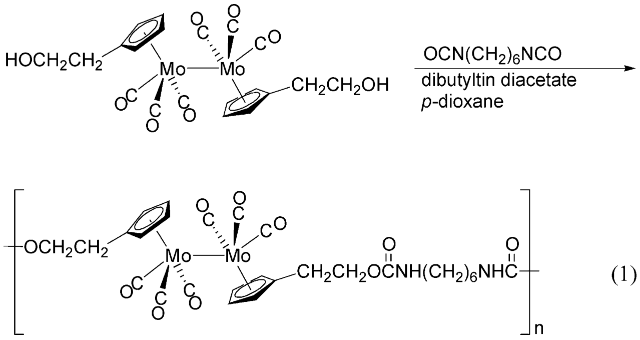
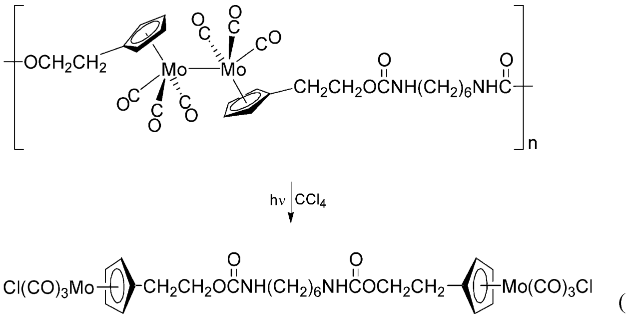
with functionally substituted cyclopentadienyl ligands, a synthetic method borrowed from earlier work on polyferrocenes.[15-21] An example of a polyurethane synthesis is shown in eq 1.[10] Thus far, polyurethanes, polyureas, polyethers, polyvinyls, polyamides, and several types of copolymers with metal−metal bonds along the backbone have been synthesized.[13] As predicted, all of these polymers are photodegradable, both in solution and in the solid state, provided that a metal-radical trap is present to capture the metal radicals and prevent reformation of the metal−metal bond by radical−radical recombination. In solution, CCl_4 or other organic halides are excellent traps, while ambient oxygen serves that purpose in the solid-state reactions.



(1)

In the case of the CCl_4 radical traps in solution, the organometallic portion of the product that forms is $(\eta^5\text{-}C_5H_4R)Mo(CO)_3Cl$ (eq 2).[13] However, the product has not been identified when oxygen is the radical trap. In this paper we report the results of experiments designed to identify the metal product that forms when oxygen is the radical trap. We also report the synthesis of a new polymer that degrades in the absence of oxygen (or any other exogenous trap) because it has Cl atoms “built in” along the backbone.



(2)

Experimental Section

Materials. Hypol 2000 was donated by the W. R. Grace Co. It was stored at 5 °C and deoxygenated with a nitrogen purge before use. Hypol 2000 is a toluene diisocyanate-endcapped, branched poly(ethylene glycol) (ca. 6.7 wt % isocyanate) with an $\overline{M}_n$ value of approximately 2000 and an equivalent weight of 625 g/equiv of isocyanate.[12,22] Tolylene 2,4-diisocyanate terminated poly(propylene glycol) (ca. 3.6 wt % isocyanate; $\overline{M}_n \approx 2300$) was obtained from Aldrich. It was stored in a nitrogen-filled drybox and used as received. 1-(Chloromethyl)-2,4-diisocyanatobenzene (97%) was obtained from Aldrich, stored in the drybox, and used as received. Poly(ethylene glycol) (PEG-1000) ($\overline{M}_n \approx 1000$) was obtained from Aldrich and deoxygenated with a nitrogen purge before use. 1,4-Butanediol (98%; Aldrich) was distilled under reduced pressure and stored under nitrogen in the drybox before use. $(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$ was prepared as previously described.[10] Dibutyltin diacetate (DBTA; Aldrich) was stored in the refrigerator in the dark and used as received. THF and hexane were refluxed with potassium under nitrogen and distilled before use. The dry THF and hexane were freeze−pump−thaw degassed at least three times before use.

Instrumentation. Infrared spectra were recorded on a Nicolet Magna 550 FT-IR spectrometer with OMNIC software. The polymerization was monitored with IR spectroscopy by scanning the solution sample from the reaction mixture and observing the changes in the IR absorption band for the isocyanate group stretching vibration. Number-average molecular weights ($\overline{M}_n$) were obtained with a Knauer vapor pressure osmometer (VPO) at 45 °C with THF as solvent. UV−visible spectra were recorded on a HP 8453 UV−visible spectrophotometer. ^1H NMR spectra were recorded on an INOVA-300 instrument in $CDCl_3$ solution. Glass transition temperatures (T_g) were measured using a TA Instruments 2920 Modulated DSC and a heating rate of 10 °C/min. Oxidation states of Mo in the photooxidation products of the polyurethanes were obtained by Kratos Hsi X-ray photoelectron spectroscopy (XPS) using the monochromatized Al source. The source was operated at 200 W. The polyurethane samples were analyzed before irradiation, after 10 min of irradiation, and after 2 h of irradiation. The vacuum in the main chamber was less than 3×10^{-9} Torr during data acquisition. To achieve optimal signal-to-noise ratios and peak widths, high-resolution spectra were acquired at 20 eV pass energy. The binding energies were referenced to the C 1s peak at 285.0 eV.

Preparation of Polymer I. Hypol 2000 (0.400 g, 0.640 mmol of −NCO) and $(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$ (0.185 g, 0.640 mmol of −OH) were added, under nitrogen, to a 100 mL Schlenk flask containing 33 mL of THF and equipped with a magnetic stir bar and condenser. DBTA (0.020 mL; 0.075 mol) was syringed into the mixture, which was then refluxed for 8 h. The reaction was monitored by IR spectroscopy. The reaction was stopped when the isocyanate band at 2273 cm^{-1} had disappeared. Absolute ethanol (0.5 mL) was added to destroy any unreacted isocyanate groups. The solution was stirred for $^1/_2$ h while cooling. Hexane (50 mL) was cannulated into the cooled solution to precipitate the polymer, which was isolated by decanting the solution and then drying under vacuum. $\overline{M}_n$(VPO, THF) = 7900 g/mol.

Preparation of Polymer II. Hypol 2000 (0.422 g, 0.675 mmol of −NCO) was placed in a 100 mL Schlenk flask equipped with a magnetic stir bar and condenser and then degassed, followed by a nitrogen purge. $(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$ (0.087 g, 0.300 mmol of −OH) and poly(ethylene glycol) (PEG-1000; 0.188 g, 0.375 mmol of −OH) were deoxygenated under nitrogen and then dissolved in 30 mL of freeze−pump−thawed, dry THF and cannulated into the Schlenk flask containing Hypol 2000. DBTA (0.020 mL, 0.075 mol) was added to the reaction solution, and the solution was refluxed for 8 h, at which time the isocyanate band at 2273 cm^{-1} had

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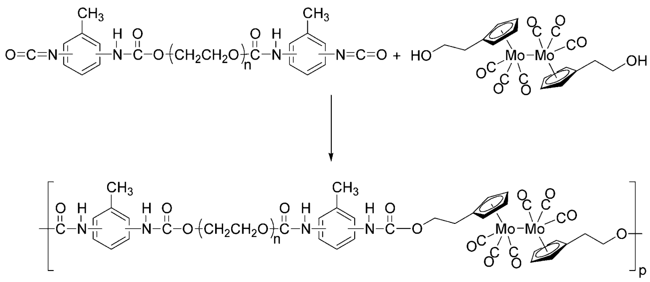
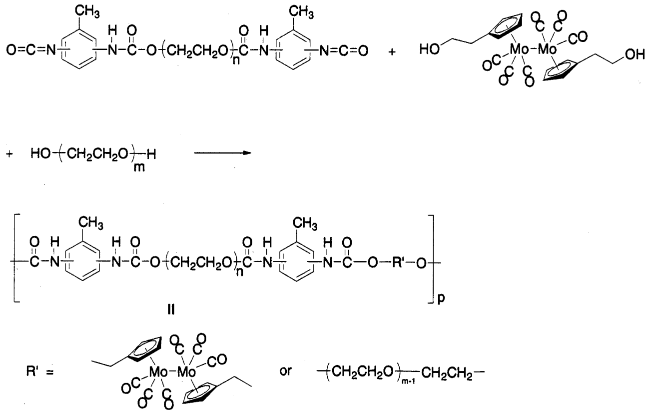
Scheme 1. Synthesis of Polymer I



I

Scheme 2. Synthesis of Polymer II



disappeared in the infrared spectrum. Absolute ethanol (0.5 mL) was added to destroy any unreacted isocyanate groups, and then the polymer was isolated and dried similarly to polymer **I**. $\overline{M}_n$(VPO, THF) = 13 500 g/mol.

Preparation of Polymer III. 1-(Chloromethyl)-2,4-diisocyanatobenzene (0.209 g, 1.94 mmol of $-NCO$), tolylene 2,4-diisocyanate terminated poly(propylene glycol) (TDI-PPG; 1.00 g, 0.857 mmol of $-NCO$), (η^5-$C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$ (0.043 g, 0.15 mmol of $-OH$), and 1,4-butanediol (0.128 g, 2.79 mmol of $-OH$) were added, under nitrogen, to a 150 mL Schlenk flask containing 50 mL of THF and equipped with a magnetic stir bar and condenser. DBTA (0.020 mL, 0.075 mmol) was syringed into the reaction mixture and the solution was refluxed for 8 h. Absolute ethanol (0.1 mL) was added, and the solution was stirred for 30 min while cooling. The solution was cast onto a Teflon surface and the solvent allowed to evaporate under an inert atmosphere for 2 days, after which time the film was thoroughly dried under vacuum. The polymer film was insoluble in all common organic solvents, and consequently, $\overline{M}_n$ could not be determined by VPO. The T_g value was determined by DSC to be −44 °C.

Results and Discussion

Syntheses and Photochemical Reactions of Polymers I and II. Polymer **I** was prepared by reacting (η^5-$C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$ with Hypol 2000 in THF solution at 50 °C (Scheme 1. As mentioned in the Experimental Section, Hypol 2000 is a toluene diisocyanate end capped, lightly branched poly(ethylene glycol). The structure was analyzed and reported in a prior paper.[12] (Note the branching feature of the prepolymer structure is not shown in Scheme 1.)

Polymer **II** was prepared in a similar fashion, except that PEG-1000 was also present (Scheme 2).

Both polymers retain the deep red color of the (η^5-$C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$ complex (λ_{max} 389 and 512 nm),[10] and both polymers form good films suitable for irradiation in the solid state. Samples of such films were prepared on glass microscope slides, and then separate samples were exposed to one of four different conditions: (1) ambient light in air, (2) ambient light under a nitrogen atmosphere, (3) air but no light, and (4) neither light nor air. Only the samples exposed to both light and air degraded, as monitored by UV−vis spectroscopy. ("Ambient light" in this instance refers to the normal light present in the laboratory from the overhead fluorescent lights and from the windows (but not direct sunlight.) These results are consistent with the results found for other polymers with metal−metal bonds along their backbones[13] and are interpreted as showing that both light and a radical trap are necessary in order for degradation to occur; i.e., a net photochemical reaction only occurs if a trapping agent is present, in this case O_2. In the absence of a trapping agent, it is proposed that the geminate (Mo, Mo) radical cage pair recombines, leading to no net reaction:[13]

$$\sim\sim\sim Mo-Mo\sim\sim\sim \xrightleftharpoons{h\nu} \sim\sim\sim Mo\bullet \ \bullet Mo\sim\sim\sim \qquad (3)$$

Thin films of the samples exposed to light and air showed interesting changes in their physical appearance. After 3−5 h of light exposure, numerous small bubbles appeared in the polyurethane films (Figures S1 and S2 in the Supporting Information). On further exposure to light, the bubbles continued to grow, eventually merging with each other to form larger bubbles. Ultimately, polymer **II** turned into a viscous liquid and dripped from the (vertical) glass microscope slide (Figure S1c). (Note that both Hypol 2000 and PEG-1000 are viscous liquids; thus, as the Mo−Mo linkers are photochemically cleaved, the PEG units are effectively regenerated, hence the formation of a liquid product.) As shown in Figure S1, the polyurethane films turned from red to brown-green during the photochemical reactions.[23]

To gain more insight into what is happening during the photodegradation reaction, the photochemical reaction of polymer **I** in air was monitored by infrared spectroscopy using a film prepared on a NaCl salt plate. During the reaction, two new bands appeared at 2170 and 2113 cm^{-1} and increased in intensity as the bubbles grew in (Figure 1). These bands agree well with those reported for gaseous CO (see Figure 1, insert),[24] and it is logical to suggest that the bubbles are formed by CO released from the Mo center during the degradation reaction. Consistent with this interpretation, the spectra show the decrease in intensity of the $\nu(C\equiv O)$ bands[11] of the $(-OCH_2CH_2C_5H_4)(CO)_3Mo-Mo(CO)_3(C_5H_4CH_2CH_2O-)$ unit at 1900, 1947, and 2004 cm^{-1} as irradiation progressed (see Figure S3 for expanded spectra of the relevant region in Figure 1). Accompanying the decrease of these bands, new bands appeared at 1771, 1865, and 2046 cm^{-1}, but continued irradiation eventually caused these bands to disappear (Figure 1 and

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[23] Mixtures of Mo(V) and Mo(VI) oxides are frequently highly colored. See, for example: Siokou, A.; Leftheriotis, G.; Papaefthimiou, S.; Yianoulis, P. *Surf. Sci.* **2001**, *482−485*(Part 1), 294.

[24] NIST Mass Spec Data Center, S. E. Stein, director, "Infrared Spectra" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P. J. Linstrom and W. G. Mallard, March 2003, National Institute of Standards and Technology: Gaithersburg, MD, 20899 (http://webbook.nist.gov).

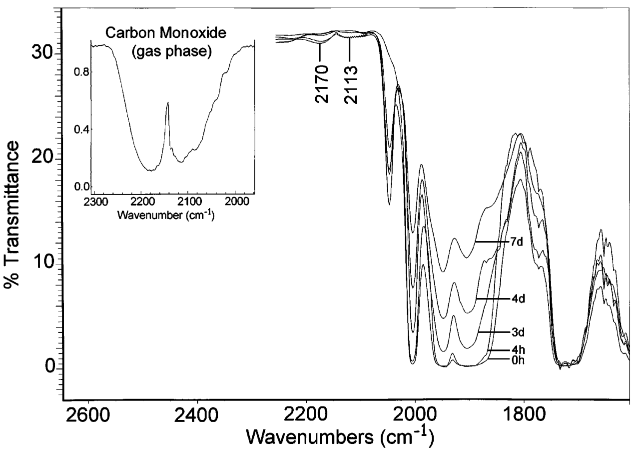


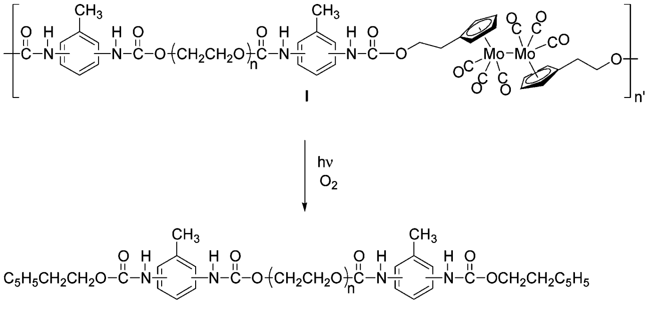
Figure 1. Infrared spectra showing the changes that occur when a film of polymer **I** on a NaCl salt plate was exposed to ambient light. The intensities of the two bands at 2170 and 2113 cm^{-1} (attributed to CO(g)) appeared and grew in intensity, the ν(C≡O) bands of the ($-OCH_2CH_2C_5H_4$)$(CO)_3$-Mo$-$Mo$(CO)_3$($C_5H_4CH_2CH_2O-$) unit at 1900, 1947, and 2004 cm^{-1} disappeared, and bands at 1771, 1865, and 2046 cm^{-1} transiently appeared and then disappeared with prolonged exposure. The inset shows the spectrum of gas-phase CO.

Figure S3). The ν(C≡O) bands at 1771, 1865, and 2046 cm^{-1} are tentatively assigned to disproportionation products of the (η^5-$C_5H_4CH_2CH_2O-$)$_2Mo_2(CO)_6$ unit. This assignment is based on the fact that, in solution, the (η^5-C_5H_5)$_2Mo_2(CO)_6$ species readily photochemically disproportionates in the presence of virtually any ligand (L) to form (η^5-C_5H_5)$(CO)_3Mo^-$ and (η^5-C_5H_5)$Mo(CO)_3L^+$ products.[25] The anionic product has bands at 1771 and 1890 cm^{-1}, while the cationic species has a band located in the 2025$-$2060 cm^{-1} region, depending on the identity of L.[25] In the photochemical reaction of the polymer, the ligand L may possibly be an oxygen donor from the polyether segment or an oxygen of a C=O group in the urethane linkage. The ionic disproportionation products are air-sensitive, and the disappearance of these bands is consistent with the eventual reaction of the ions with oxygen to form metal oxide final products that contain no CO ligands.

X-ray Photoelectron Spectroscopic Investigation. To identify the fate of the Mo in the photochemical degradation reactions of the polyurethanes, samples of the polymers were analyzed by X-ray photoelectron spectroscopy (XPS). Figure S4 (Supporting Information) shows XPS spectra in the Mo 3d region for polymer **I** exposed to ambient light for different periods of time. XPS spectra of (η^5-$C_5H_4CH_2CH_2OH$)$_2Mo_2(CO)_6$ and MoO_3 are also shown for comparison. The Mo 3d core level presents two peaks, $3d_{3/2}$ and $3d_{5/2}$, due to spin$-$orbit splitting, and accordingly the spectra were fit to two peaks. The binding energy difference between the $3d_{3/2}$ and $3d_{5/2}$ peaks (3.1 eV) and peak intensity ratios ($I(3d_{5/2})/I(3d_{3/2}) = 3/2$) were kept constant for all of the fits. The Mo $3d_{5/2}$ binding energies and the corresponding content in the sample surface are listed in Table 1. (The $3d_{5/2}$ peak is listed in the table because it is the most intense of the two peaks.) The values have been corrected for the effects of charge neutralization.

Note that the unexposed polymer **I** has essentially the same binding energy (229.1 eV) as (η^5-$C_5H_4CH_2CH_2$-OH)$_2Mo_2(CO)_6$ (228.9 eV), consistent with the unexposed polymer still having intact ($-OCH_2CH_2C_5H_4$)$(CO)_3$Mo$-$Mo$(CO)_3$($C_5H_4CH_2CH_2O-$) units with Mo in the +1 oxidation state. (The slight shift in binding energies between the two samples may be attributed to a slightly different chemical environment of Mo in the polymer compared to that in the solid microcrystals.) After exposure to ambient light for 10 min, a sample of the polymer showed $3d_{5/2}$ peaks at 229.1 eV (Mo(I) in the undegraded polymer) and at 231.5 eV. On the basis of literature data, the oxidation state of Mo in the latter species is likely +5.[26,27] The ratio of Mo(I) to Mo(V) is 74% to 26%. After further exposure to ambient light for 2 h, the XPS spectrum showed a major peak at 232.9 eV (assigned to a Mo(VI) species) and a smaller peak at 231.7 eV. The latter peak is again assigned to Mo(V). No peaks were present that could be assigned to undegraded Mo(I). The ratio of Mo(VI) to Mo(V) was 80% to 20%.

Photochemical Reactivity of the Polyurethanes in Air. The key results in the sections above are (1) the Mo$-$Mo bond disappears in the photochemical reaction of the polymers (as demonstrated by the disappearance of the ν(C≡O) bands for the ($-OCH_2CH_2C_5H_4$)$(CO)_3$-Mo$-$Mo$(CO)_3$($C_5H_4CH_2CH_2O-$) unit and by the color change of the films), (2) CO is released in the photochemical reactions (as demonstrated by the appearance of bubbles in the films and the infrared spectrum of free CO), (3) no other Mo$-$carbonyl species is formed as a final product, (4) O_2 is necessary to obtain a net photochemical reaction, (5) the ultimate fate of the Mo is a Mo(VI) species, and (6) the fate of the organic portion of the polymers is a low-molecular-weight liquid, likely PEG units. Taken together, these results suggest the photochemical reaction shown in eq 4 (shown for polymer **I**, but an analagous reaction applies for polymer **II**).



(4)

Photodegradation of Polymer III under an N_2 Atmosphere. A long-range goal is to develop ways to control the rate of degradation in photodegradable polymers.[13] One approach is to control the efficiency with which any photogenerated metal radicals are captured. (The capture efficiency will affect the rate of degradation, because the radicals can back-react to re-form the metal$-$metal bond.) To control the rate of the

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[26] Werfel, F.; Minni, E. *J. Phys. C: Solid State Phys.* **1983**, *16*, 6091.

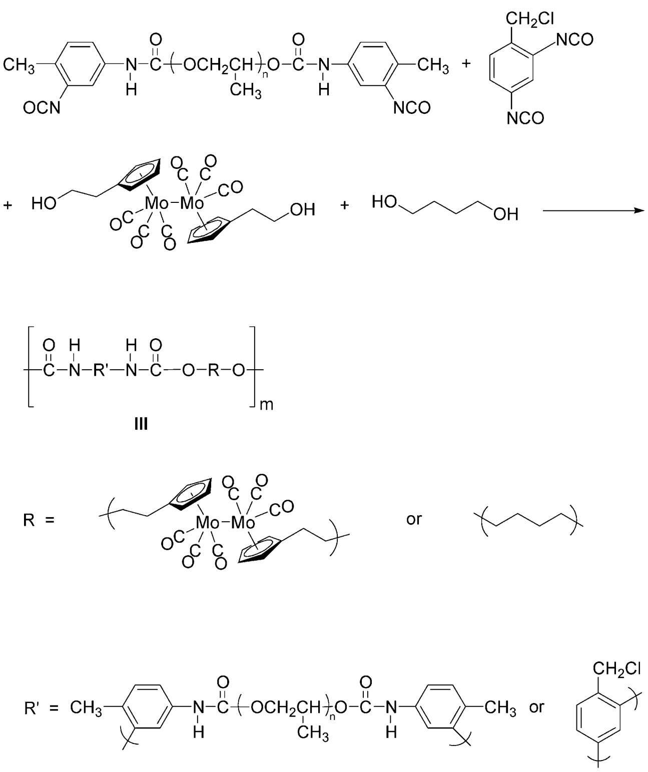
[27] Xie, G.; Jiang, Z. *Chin. Sci. Bull.* **2000**, *45*, 1562.

Table 1. Mo $3d_{5/2}$ Binding Energy of Different Materials[a]

material	Mo $3d_{5/2}$ binding energy (eV)[b]				
	Mo(0)	Mo(+1)	Mo(+4)	Mo(+5)	Mo(+6)
pure Mo (Mo(0))	227.8				
MoO_2 (Mo(IV))			229.7		
MoO_3 (Mo(VI))					232.7
(η^5-$C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$ (Mo(I))		228.9			
polymer **I**					
no exposure to light		229.1			
after 10 min exposure		229.1 (74%)		231.5 (26%)	
after 120 min exposure				231.7 (20%)	232.9 (80%)

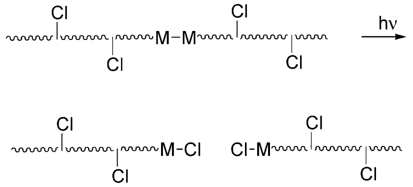
[a] C 1s hydrocarbon = 285.0 eV. [b] The percentages listed next to the binding energies are the percentages of the total $3d_{5/2}$ peak area accounted for by that peak.

Scheme 3. Synthesis of Polymer III



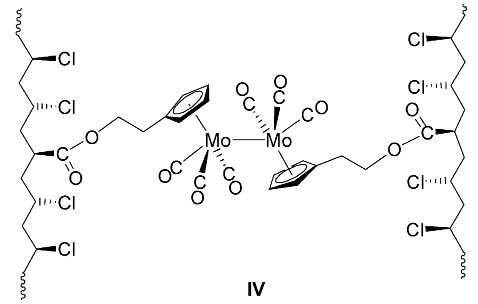
radical trapping reaction, we are designing polymers with radical traps built into the backbone. It is suggested that it should be possible to control more easily the degradation of polymers with built-in radical traps, because the concentration of the trap can be manipulated. In a prior paper we reported the photochemical degradation reactions of a PVC polymer modified with Mo−Mo bonds.[28] To explore the effect of a lower concentration of Cl, polymer **III** was synthesized (Scheme 3).

The photochemical reaction of polymer **III** (λ = 546 nm) under a nitrogen atmosphere was monitored by infrared and electronic absorption spectroscopy. The latter method showed the disappearance of the absorption band at 512 nm, and infrared spectroscopy showed the disappearance of the ν(C≡O) bands in the ($-OCH_2CH_2C_5H_4)(CO)_3Mo-Mo(CO)_3(C_5H_4CH_2CH_2O-)$ unit at 2005, 1950, and 1907 cm^{-1} and the appearance of new bands at 2048 and 1972 cm^{-1}, attributable to the ($-OCH_2CH_2C_5H_4)Mo(CO)_3Cl$ component.[28,29] The reaction is shown in sketch form in eq 5.



(5)

The quantum yield for the reaction of polymer **III** was determined to be 0.35. Perhaps surprisingly, this quantum yield is higher than the quantum yield (0.15) for the similar reaction of the modified PVC polymer **IV**,[28]



IV

which has a considerably higher concentration of C−Cl bonds for metal-radical trapping. These values can also be compared to the quantum yield (0.36) of plasticized **IV**.[30] One possible explanation is the difference in T_g values of the polymers. The irradiation of the polymers was performed at 25 °C, which is below the T_g value of polymer **IV** (65 °C) and above the T_g values of polymer **III** (−44 °C) and plasticized polymer **IV** (20 °C). It is suggested that chain movement to achieve proper orientation for radical capture and C−Cl concentration are both important factors in determining the efficiency of photochemical degradation.

Key Insights and Conclusions. Films of polymers containing the ($-OCH_2CH_2C_5H_4)(CO)_3Mo-Mo(CO)_3(C_5H_4CH_2CH_2O-)$ unit along their backbones react photochemically with visible light in the presence of oxygen to form Mo(V) and Mo(VI) oxides, CO(g), and lower molecular weight organic-backbone polymer species. In the absence of metal-radical traps (e.g., O_2), no net photochemical reaction occurs, because the photo-

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(28) Chen, R.; Yoon, M.; Smalley, A.; Johnson, D. C.; Tyler, D. R. *J. Am. Chem. Soc.* **2004**, *126*, 3054.

(29) The band at 1972 cm^{-1} was merged into the strong absorption from the parent dimer.

(30) Chen, R.; Tyler, D. R. *Macromolecules* **2004**, *37*, 5430.

generated Mo radicals recombine. Polymer **III** contains built-in radical traps (C−Cl bonds), and this polymer efficiently degrades in the absence of oxygen, because the Mo radicals abstract the Cl atoms to form Mo−Cl bonds, thus preventing the recombination reactions of Mo radicals. Despite the relatively low concentration of C−Cl bonds in polymer **III**, it degrades more efficiently at room temperature than polymers containing considerably higher concentrations of C−Cl bonds. It is proposed that, because T_g is lower than room temperature in polymer **III**, chain movement to achieve the proper orientation for the abstraction reaction is relatively facile, resulting in a relatively efficient photochemical reaction.

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Supporting Information Available: Figures showing the changes that occur in films of polymers **I** and **II** on exposure to ambient light, infrared spectra showing changes in the region 2200−1700 cm^{-1} of polymer **I** degraded in air with ambient light, XPS spectra of the Mo 3d core levels for polymer **I** following exposure to light for various times, and XPS spectra of (η^5-$C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$ and MoO_3. This material is available free of charge via the Internet at http://pubs.acs.org.

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