Macromolecules 1993, 26, 3485-3489

Photodegradation of α-Olefin/Carbon Monoxide Alternating Copolymer

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Received January 25, 1993; Revised Manuscript Received April 5, 1993

ABSTRACT: The anaerobic photodegradation behaviors of bulk alternating copolymers of propylene/carbon monoxide (CO) and ethylene/CO have been studied by irradiation with 2537-Å light. Photolysis of the former resulted in weight loss, molecular weight depression, cross-linking, and the formation of hydroxyl and terminal vinyl groups. The room temperature quantum yields of chain scission and Norrish type II reactions were found to be 0.015 ± 0.002 and 0.011 ± 0.002, respectively. Ethylene/CO alternating copolymer does not undergo Norrish type II photolysis because of the absence of γ-hydrogens. Even the Norrish type I processes occur with low probability probably because of the strong "cage effect" and reactivity of the primary radicals produced.

Introduction

Several Pd(II) systems have been reported[1-5] which catalyze the perfectly alternating copolymerization of ethylene (E) with carbon monoxide (CO) to yield polyketone $[C(O)CH_2CH_2]_n$ or E/CO alternating copolymer. Recently, propylene (P) and CO have been polymerized into semicrystalline alternating copolymers[6-8] or into amorphous copolymers.[6,7,9] These polymers exhibit unusual physicomechanical properties and have the potential for further functionalization.[2e,3] The low monomer cost enhances the commercial attractiveness for these materials.

The ketone group C=O contained in the olefin/CO alternating copolymer is a photoactive chromophore. Packaging material fabricated from a bio- or photodegradable polymer[10] is deemed more friendly to the environment. Nonalternating E/CO copolymer of low CO content such as the 0.99/0.01 E/CO material had been marketed as Ecoplastics. It has been shown that ketones in polymeric materials undergo some of the same photochemical reactions as low molecular weight ketones.[11-15] Norrish type I and type II reactions (Scheme Ia,b) are the main pathways. A third primary process, which produces a cyclobutanol product (Scheme Ic),[16] had been identified for a few ketones. Extensive studies have also been carried out on photodegradation behaviors of polymers containing ketonic pendant groups.[15]

The purpose of this study is to investigate the photolysis mechanisms of ethylene and propylene carbon monoxide alternating copolymers. Significant differences were found between the two materials.

Experimental Section

Materials. The alternating copolymers were prepared by polymerizations of α-olefin and CO catalyzed by $[(Ph_2P(CH_2)_3PPh_2)\ Pd^{2+}\cdot 2BF_4^-]$ as described previously.[6,7] The standard copolymerization conditions for propylene/CO are as follows: catalyst (0.02 mmol), methanol (1 mL), 1,2-dichloroethane as solvent (150 mL), 60 psig propylene, 540 psig CO, at 50 °C for 4 h. A 300-mL Paar reactor was dried and purged with argon, and then the catalyst, methanol, and solvent were cannulated into it. Propylene and carbon monoxide were introduced in turn. The mixture was heated to the polymerization temperature. At the end of a copolymerization the unreacted monomers were vented, and the copolymer was purified by precipitation with methanol and dried in vacuo at ambient temperature for 24 h. Most chain end groups of propylene/CO alternating copolymer are $-C(O)OCH_3$ types, with a small proportion of chain end groups being $CH_3CH{=}CHCOP$ and $CH_2{=}C(CH_3)COP$. They are different from the Norrish type II photolysis product which is $CH_2{=}CHCOP$ (*vide infra*). The copolymerization conditions for ethylene/CO are similar to those of propylene/CO, with 300 psig ethylene, and 300 psig CO. After unconsumed monomers were vented, the insoluble alternating copolymer was filtered and washed with methanol. The polymer was dried in vacuum for 24 h.

The solid-state ^{13}C NMR spectrum of E/CO alternating copolymer is shown in Figure 1. There are only two peaks: one is attributed to the carbonyl carbon; the other is the methylene carbon. This spectrum proves the alternating molecular structure of $(-CH_2CH_2C(O)-)_n$.

The solution ^{13}C NMR spectrum of P/CO alternating copolymer is given in Figure 2. The assignments of this spectrum have been made by us and other investigators;[8,9] the general structure is $(-C(O)CH_2CH(CH_3)-)_n$. The intense carbonyl IR band was located around 1700 cm^{-1} (Figure 3).

Polymer Characterization. The molecular weight of the degraded polymer was determined by Waters GPC using $CHCl_3$ as solvent. The GPC column used was Jordi 500 Å which was specifically designed for low molecular weight (100-25 000) measurement. Infrared spectra of the polymers, both before and after photolysis, were run on a Nicolet IR/32 FTIR spectrometer, using the thin films (vide infra). DSC was performed on a Du Pont 2000 thermoanalysis system with a 20 °C/min heating rate. The ultraviolet spectra were taken on a Perkin-Elmer Lambda Array 3840 UV spectrophotometer.

A solution ^{13}C NMR spectrum was recorded on a Varian XL-300 spectrometer using $CDCl_3$ as solvent. A solid-state ^{13}C NMR spectrum was obtained at 50 MHz on an IBM AF200 spectrometer. Both magic angle spinning and cross-polarization were employed to achieve satisfactory resolution.

Photolysis. A RPR-100 Rayonet photochemical chamber manufactured by the Southern New England Ultraviolet Co. was used in this study. The intensity of the 2537-Å light was measured by using uranyl oxalate actinometry.[17] The result of the light intensity calibration was in close agreement with the intensity reading supplied by the company.

A thin film of alternating copolymer was photolyzed. P/CO copolymer film was prepared by solvent casting of copolymer (10.5 mg) dissolved in chloroform onto a 25 × 4 mm NaCl salt and dried to constant weight. E/CO copolymer film was made by compression molding.

A quartz cell, 3.5 cm in diameter and 5 cm high, was constructed to enable measurement in the absence of oxygen. The cell was purged with argon in all the photochemical reactions. The ultraviolet spectrum of each sample was recorded before photolysis to determine the optical density of the alternating copolymer film.

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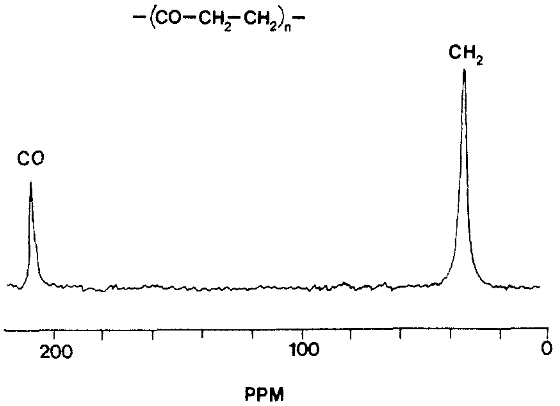


Figure 1. Solid-state ^{13}C NMR spectrum of E/CO alternating copolymer.

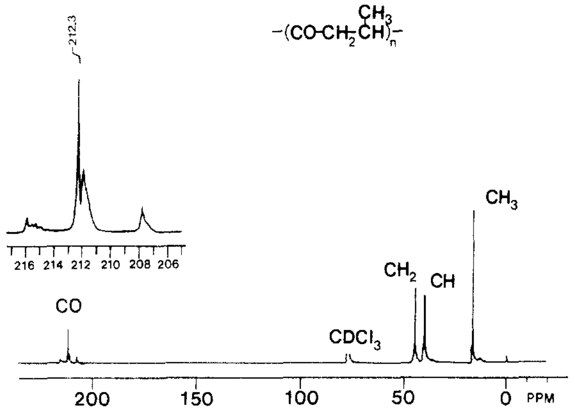


Figure 2. ^{13}C NMR spectrum of the P/CO alternating copolymer made by catalyst [$(Ph_2P(CH_2)_4PPh_2)Pd^{2+}\cdot 2BF_4^-$] at 0 °C.[6] $CDCl_3$ was used as the solvent.

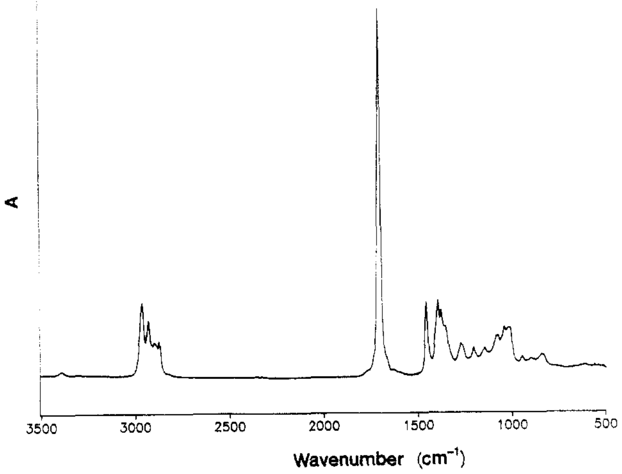


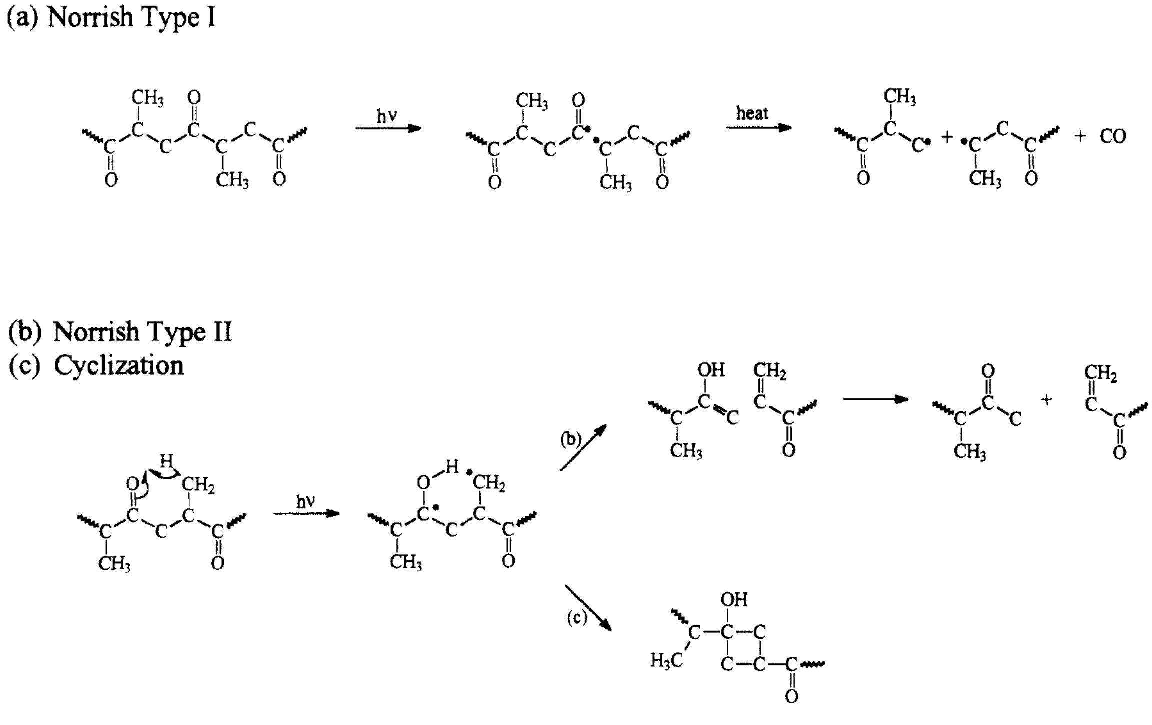
Figure 3. IR absorbance spectrum of P/CO alternating copolymer.

Results and Discussion

Photolysis of the P/CO copolymer results in a decrease in molecular weight and weight loss. NMR was found to be unhelpful in monitoring the photodegradation. ^{13}C NMR is too low in sensitivity. Each P/CO copolymer film weighs only 10.5 mg. Forty films have to be irradiated and combined for NMR spectral analysis. The meaningfulness of such measurements is questionable. ^{1}H NMR is in principle a useful technique. The copolymer is known to have $CH_3CH{=}CHC(O)$– (I) and $CH_2{=}C(CH_3)CO$– (II) end groups. The Norrish type II product will have the end group $CH_2{=}CHCO$– (III). In the virgin polymer neither I nor II was detectable with 50× sensitivity. After 20 min of UV exposure, weak resonances at 5.1–5.6 ppm were detected with high gain. The S/N ratio is so poor that measurement has no quantitative value.

The infrared spectrum of the degraded polymer shows an increase in the absorbance at 11.0 μm (912 cm^{-1}, Figure 4), which was also observed by Hartley and Guillet[18] in the photolyzed 0.99/0.01 E/CO copolymer. They assigned this band to terminal vinyl double bonds $RCH{=}CH_2$. There was also an increase in the absorbance around 3480 cm^{-1}, characteristic of the –OH group as depicted in Figure 5. The absorbance at 3400 cm^{-1} is assigned to the overtone of the C=O stretching frequency. The photolyzed P/CO copolymer has a UV spectrum shifted to long wavelength as compared to the virgin material (Figure 6). This red shift may be attributed to the formation of an α,β-unsaturated ketone, $CH_2{=}CHC(O)P$.

Scheme I



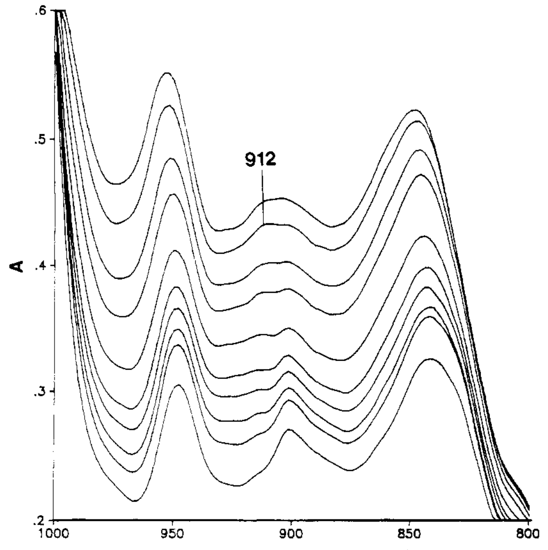


Figure 4. IR absorbance spectra (800–1000-cm^{-1} region) of degraded P/CO alternating copolymers. The curves from bottom to top reperesent the spectra of the polymer having 0, 10, 20, 30, 40, 60, 90, 120, 180, and 240 min of UV exposure.

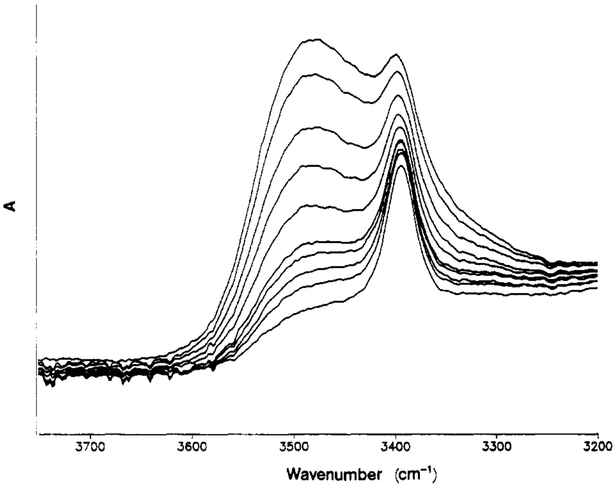


Figure 5. IR absorbance spectra (3200–3750-cm^{-1} region) of degraded P/CO alternating copolymers. The curves from bottom to top represent the spectra of the polymers having 0, 10, 20, 30, 40, 60, 90, 120, 180, and 240 min of UV exposure.

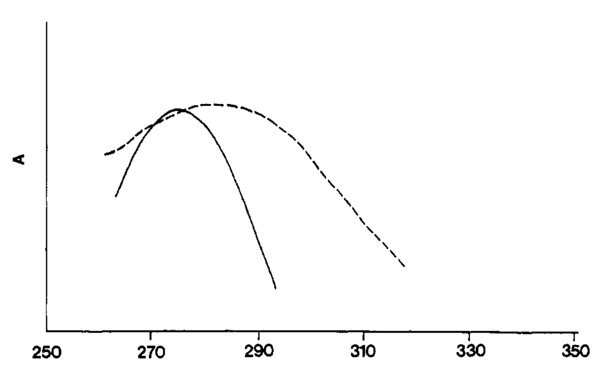


Figure 6. UV spectra of P/CO polymers having 0 (solid line) and 120 (dotted line) min of UV exposure.

The above results are consistent with the degradation mechanism for the P/CO copolymer based on the Norrish type I and type II reactions (Scheme I). The former produces radicals (Scheme Ia) and evolves carbon monoxide, whereas the latter (Scheme Ib) yields a ketone and a terminal vinyl group. Both processes cause main-chain scission and reduction of MW. The weight loss is mainly due to the elimination of CO following the Norrish type I process.

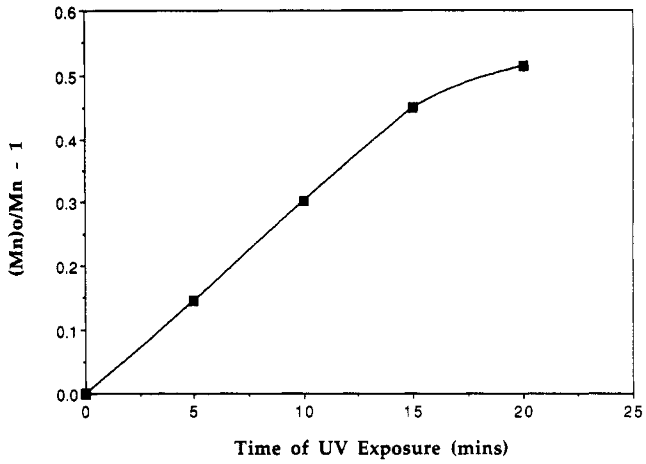


Figure 7. Number of backbone chain scissions as a function of the UV exposure time during photolysis of bulk P/CO alternating copolymer at ambient temperation: 10.5 mg of polymer was cast on the 25 × 4 mm NaCl plate; film thickness = 1.8 × 10^{-3} cm; intensity of the light absorbed = 8.0 × 10^{6} einstein/g·s or 1.7 × 10^{-8} einstein/cm^2·s. $(M_n)_0$ = 4170.

If $(M_n)_0$ is the number-average molecular weight of the starting material, and M_n is the number-average molecular weight of the degraded polymer, then $[(M_n)_0/M_n - 1]$ is equal to the average number of polymer bonds severed per initial polymer molecule. Therefore, the quantum yield of chain scission (ϕ_{sc}) can be calculated by using eq 1.

$$\phi_{sc} = \{d[(M_n)_0/M_n - 1]/d(I_a t)\}[W/(M_n)_0] \qquad (1)$$

where I_a is absorbed light intensity per second, t is time in seconds, and W is the initial weight of the polymer. Figure 7 shows the increase in $[(M_n)_0/M_n - 1]$ as the photolysis progresses. It can be seen that the rate of bond breaking is initially linear but slows down as the reaction proceeds. Knowing the amount of light absorbed by calibration and using the initial slope of the curve in Figure 7, we calculated the quantum yield of chain scission for bulk P/CO copolymer to be 0.015 ± 0.002 at ambient temperature.

Hartley and Guillet[18] had proposed an explanation for the observed decrease in the rate of chain scission with the progress of photolysis. One of the Norrish type II reaction products is a polymer chain which terminates in a $CH_3C(=O)$– group. The concentration of these groups increases as the photolysis proceeds; the photoreaction of these groups by either type I or type II reaction would produce no detectable change in the molecular weight. Besides this apparent reason, we can offer another explanation which is probably more important here. The radicals generated by type I reaction will cause crosslinking in the copolymer which in turn will slow down the depression of molecular weight. In the later stage of the photolysis, the molecular weight will even increase. This explanation was evidenced by the fact that the P/CO thin film became partially insoluble in any organic solvent after 30 min of UV exposure, while the films irradiated for 5, 10, 15, and 20 min could be easily dissolved in the chloroform.

The infrared absorbance of the degraded polymers at 912 cm^{-1} (11.0 μm), characteristic of vinyl double bonds, is expressed as the absorbance, A, in eq 2. where b is the

$$A = \epsilon bc \qquad (2)$$

film thickness, c is the concentration of the terminal vinyl double bond in bulk P/CO copolymer, and ϵ is the

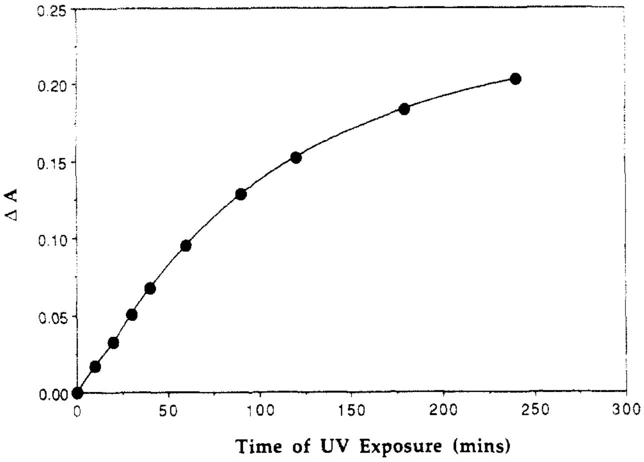


Figure 8. Increase in the absorbance at 912 cm^{-1} (11.0 μm) as a function of the UV exposure time during photolysis of bulk P/CO alternating copolymer. The data are taken from Figure 3: 10.5 mg of polymer was cast on the 25 × 4 mm NaCl plate; film thickness = 1.8×10^{-3} cm; intensity of the light absorbed = 8.0×10^{-6} einstein/g·s or 1.7×10^{-8} einstein/cm^2·s.

extinction coefficient for the vinyl double bond produced in type II reaction. We can further write

$$\Delta A_1/\Delta A_2 = b_1c_1/b_2c_2 \qquad (3)$$

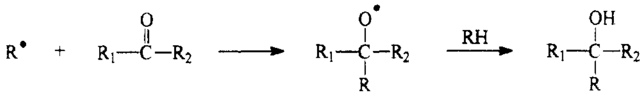
Figure 8 is the plot of ΔA vs time of UV exposure; the data are taken from Figure 4. The curve shows an increase in the absorbance at 912 cm^{-1} with the progress of photolysis. Using the initial rate and a set of A, b, and c,[18] a value of c^2 for the vinyl double bond molar concentration in P/CO polymer at a given time of UV exposure could be calculated. The quantum yield for vinyl double bond production or of Norrish type II reaction, ϕ_{II}, was thus determined to be 0.011 ± 0.002 in solid phase at ambient temperature.

Similar to the rate of chain scission, the rate of vinyl double bond production slows down in the later stage of the photolysis, possibly due to the reaction of the olefinic species with radicals generated in the type I reaction.[18]

The similarity of the values of ϕ_{II} and ϕ_{cs} for P/CO copolymer indicates that most of the chain scissions are the result of the Norrish type II process. Norrish type I reaction contributes very little (<25%) to the backbone scission. The low quantum efficiency of the latter can be explained by the "cage effect".[19,20] Radical pairs produced by photolysis or thermolysis either can recombine within the cage at the site of their formation, which is about one molecular diameter in dimension or can be separated by diffusion. The fraction of the former event, "cage recombination", increases with an increase in the viscosity of the medium. Therefore, the efficiency of cage recombination of the radical pair generated by Norrish type I is higher in bulk P/CO copolymer than in liquid medium and is even greater in highly crystalline E/CO copolymer[21] (*vide infra*). Conversely, the quantum efficiencies of chain scission following the Norrish type I process decrease in this order.

It is interesting to compare the ϕ_{II} of P/CO alternating copolymer to the ϕ_{II} of 0.99/0.01 E/CO copolymer studied by Hartley and Guillet. Their result showed $\phi_{\mathrm{II}} = 0.025 \pm 0.003$ for the 0.99/0.01 E/CO copolymer in the solid phase. Both materials have T_g much lower than the ambient temperature; the T_g of P/CO copolymer was measured to be −8 °C.[6] So, at the ambient temperature, as was shown for the 0.99/0.01 E/CO copolymer,[18] ϕ_{II} is independent of temperature provided it is higher than T_g. A possible explanation for the higher ϕ_{II} of 0.99/0.01 E/CO copolymer than that of the P/CO copolymer may be due to the difference between the two types of γ-hydrogen atoms abstracted in their photolysis. The type II reaction involves abstraction of hydrogen to form a biradical (Scheme Ib); the relative reactivities would be expected to be sensitive to the substitution at the γ-carbon atoms.[22] Ausloos[23] found that there is a 13/1 preference for attack on the secondary position in 4-methyl-2-hexanone for the type II reaction. Nicol and Calvert[24] showed that $\phi_{\mathrm{II4a}}/\phi_{\mathrm{II4b}}$ (see eq 4) of the 4-octanone is 7/1.

Scheme II



$$\mathrm{R^{\bullet}} + \mathrm{R_1{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R_2} \longrightarrow \mathrm{R_1{-}\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle O^{\bullet}}{|}}{C}}{-}R_2} \xrightarrow{\mathrm{RH}} \mathrm{R_1{-}\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}R_2}$$

$$n\mathrm{C_3H_7(O{=})C}{-}n\mathrm{C_4H_9} \rightarrow n\mathrm{C_3H_7(O{=})CCH_3} + \mathrm{C_3H_6} \qquad (4a)$$

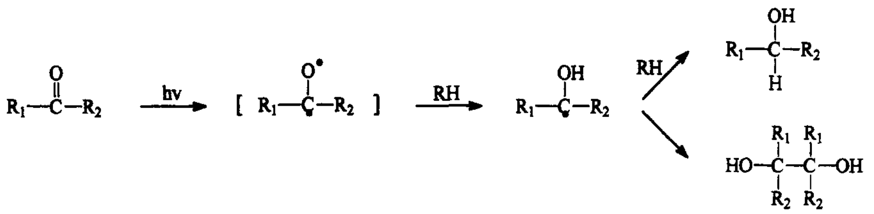
$$\rightarrow \mathrm{CH_3(O{=})C}{-}n\mathrm{C_4H_9} + \mathrm{C_2H_4} \qquad (4b)$$

They also showed that the total ϕ_{II} of 4-octanone is 1.8 times larger than the total ϕ_{II} for 4-heptanone. Wagner and Hammond[22] performed quenching experiments which demonstrated that the abstraction of a secondary γ-hydrogen atom was easier than the abstraction of a primary γ-hydrogen. In the 0.99/0.01 E/CO polymer, each carbonyl group was separated on the average by 200 methylenes. Therefore, it is a secondary γ-hydrogen being abstracted by the carbonyl carbon in type II reaction. For P/CO copolymer, however, the primary γ-hydrogen will be abstracted due to the alternating structure. The above argument justifies the higher ϕ_{II} of 0.99/0.01 E/CO copolymer than that of the P/CO alternating copolymer. There is another trivial factor which may contribute to the difference between the two ϕ_{II}'s. The P/CO copolymer was irradiated by a 2537-Å lamp, while the 0.99/0.01 E/CO copolymer was photolyzed by 3130-Å light.

The observance of the –OH group (Figure 5) during the photolysis of P/CO copolymer may be attributed to the formation of serveral types of alcohol. An alternative pathway for the Norrish type II process is the combination of radicals following H abstraction. Cyclobutanol could be formed as the result of the cyclization (Scheme Ic). Scheme II is another pathway which may produce an alcohol. Radicals produced in the type I reaction can attack a carbonyl carbon; the resulting alkoxy radical subsequently abstracts a hydrogen atom to form tertiary alcohol. The major difference between these two processes is that Scheme Ic is intramolecular, while Scheme II is intermolecular. A third possible process which can generate an alcohol is depicted in Scheme III. The necessary condition for this process to occur is the presence of good hydrogen donors. If the keto radicals are present at high enough concentrations or have long lifetimes, they may combine to form pinacols.[17] The relative contributions of these three processes may be revealed by studing the photolysis of E/CO alternating copolymer.

The absence of the IR absorption peak around 900 cm^{-1} for the E/CO copolymer after 1 h of UV irradiation indicates no vinyl double bonds were formed; therefore, Norrish type II reaction did not occur. This is expected because there is no γ-hydrogen in the polymer. Figure 9 shows that there is an increase of absorbance around 3480 cm^{-1} for E/CO polymer with 1 h of UV exposure, which indicates the formation of an –OH group. Since the E/CO alternating copolymer lacks a γ-hydrogen, the process shown in the Scheme Ic is not suitable for accounting for the formation of an –OH group. Furthermore, the biradical generated in Scheme III would prefer to undergo radiationless relaxation because the polymer is a poor hydrogen donor. Therefore, the –OH group in E/CO copolymer is

Scheme III



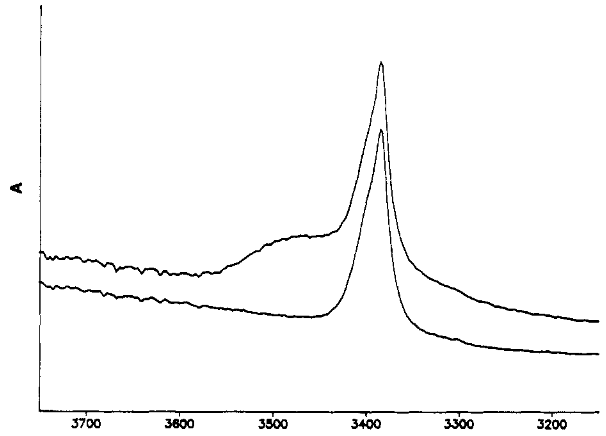


Figure 9. IR absorbance spectra (3150–3750-cm^{-1} region) of the E/CO alternating copolymers having 0 (bottom curve) and 60 (top curve) min of UV exposure.

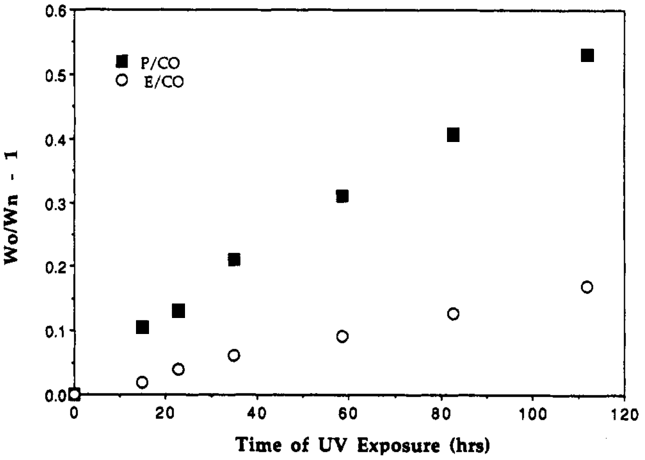


Figure 10. Increase of the weight loss of P/CO copolymer (solid square) and E/CO copolymer (unfilled circle) as a function of the UV exposure time during photolysis in the solid phase: 38 mg of P/CO and E/CO polymers were compression-molded under the same pressure. The resulting two films have diameters of 1.9 cm.

more likely to be produced by the process given in Scheme II. If P/CO copolymer behaves similarly, we expect the process described in Scheme II to be the source for the –OH production in P/CO as well. Obviously, more rigorous proof is needed to make a firm conclusion.

The weight loss behaviors of P/CO and E/CO copolymers are shown in Figure 10 by plotting ($W_0/W_n - 1$) vs time of UV exposure (W_0, original weight; W_n, degraded polymer weight). The rate of weight loss for the P/CO copolymer is about 3 times as fast as that for E/CO copolymer, which suggests that the Norrish type I reaction rate for P/CO is faster than that for E/CO. There is a ready explanation for this phenomenon. The type I reaction of E/CO copolymer generates primary radicals, situated in strong cages of a crystalline E/CO copolymer environment. Cage recombination is more probable than a similar event in the P/CO copolymer. Therefore, the net quantum yield of type I reaction for E/CO copolymer is lower than that for the P/CO copolymer.

Some Pd complexes are photoactive. It is not possible to remove all catalyst residues from the alternating copolymers. The effect of these residues on photolysis has been considered. We used 0.02 mmol of Pd catalyst to produce 5.7 g of P/CO copolymer. Therefore, the mole ratio of the repeat unit $-CH_2CH(CH_3)C(O)-$ to the Pd catalyst is $4.1 \times 10^3/1$ (the actual ratio is greater than this because some catalysts may dissolve in the methanol when the polymer was precipitated with methanol). The Pd catalyst may absorb the light and, therefore, reduce the ϕ_{II} of copolymer. However, neither the amount nor the structure of the catalyst residue is known. So we added 0.04 mmol of Pd catalyst to 5.7 g of methanol precipitated P/CO copolymer and solvent casted into films. The ϕ_{II} for this material was found to be 9.7×10^{-3}, which is within experimental error of $\phi_{II} = 0.011 \pm 0.002$ for the copolymer without catalyst added intentionally. Therefore, any Pd residues have no measurable effect on the photodegradation of the P/CO alternating copolymer.

Acknowledgment. This work was supported by the Center for University of Massachusetts Industry Research on Polymers and benefitted by the Central Facilities of the Materials Research Laboratories.

References and Notes

(1) Reppe, W.; Magin, A. U.S. Patent 2,577,208, 1951.
(2) (a) Sen, A.; Lai, T. W. *J. Am. Chem. Soc.* **1982,** *104,* 3520. (b) Lai, T. W.; Sen, A *Organometallics* **1984,** *3,* 866. (c) Sen, A. *CHEMTECH.* **1986,** 48. (d) Jiang, Z.; Sen, A. *Macromolecules* **1992,** *25,* 880. (e) Sen, A.; Jiang, Z.; Chen, J.-T. *Macromolecules* **1989,** *20,* 2012. (f) Sen, A. *Adv. Polym. Sci. 73/74,* 125.
(3) Drent, E.; van Brockhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991,** *417,* 235.
(4) (a) Fenton, D. M. U.S. Patent 3,530,109, 1970. (b) Nozaki, K. U.S. Patent 3,689,460, 1972; 3,835,123, 1974. (c) Shryne, T. M. U.S. Patent 3,948,388, 1976.
(5) Zhao, A. X.; Chien, J. C. W. *J. Polym. Sci., Part A* **1992,** *30,* 2735.
(6) Xu, F. Y.; Chien, J. C. W. *Makromol. Chem.,* in press.
(7) Chien, J. C. W.; Zhao, A. X.; Xu, F. *Polym. Bull.* **1992,** *28,* 315.
(8) Batistini, A.; Consiglio, G.; Suter, U. W. *PMSE Prepr.* **1992,** *67,* 104.
(9) Jiang, Z.; Dahlen, G. M.; Houseknecht, K.; Sen, A. *Macromolecules* **1992,** *25,* 2999.
(10) Bremer, Y. P. *Polym. Plast. Technol. Eng.* **1982,** *18,* 137.
(11) Guillet, J. E.; Dhanraj, J.; Golemba, F. J.; Hartley, G. H. *Adv. Chem. Ser.* **1986,** *85,* 272.
(12) Heskins, M.; Guillet, J. E. *Macromolecules* **1968,** *1,* 97.
(13) Golemba, F.; Guillet, J. E. *Macromolecules* **1972,** *5,* 212.
(14) Amerik, Y.; Guillet, J. E. *Macromolecules* **1971,** *4,* 375.
(15) Guillet, J. E. *Polymer Photophysics and Photochemistry* Cambridge University Press: Cambridge, U.K., 1985.
(16) Yang, N. C.; Yang, D. H. *J. Am. Chem. Soc.* **1958,** *80,* 2913.
(17) Leighton, W. G.; Forbes, G. S. *J. Am. Chem. Soc.* **1930,** *52,* 3139.
(18) Hartley, G. H.; Guillet, J. E. *Macromolecules* **1968,** *1,* No. 2, 165.
(19) Franck, J.; Rabinowitch, E. *Trans. Faraday Soc.* **1934,** *30,* 120.
(20) Noyes, R. M. *Prog. React. Kinet.* **1961,** *2,* 129.
(21) Even if the "cage effect" is strong for E/CO, some radicals generated from Norrish type I reaction still can diffuse out of the "cage" which is evidenced by weight loss of E/CO upon UV exposure. Those diffused radicals can react with polymer to form the –OH group (Scheme II). The quantum yield for this process is very small.
(22) Wagner, P. J.; Hammond, G. S. *J. Am. Chem. Soc.* **1965,** *87,* 4009.
(23) Ausloos, P. *J. Phys. Chem.* **1961,** *65,* 1616.
(24) Nicol, C. H.; Calvert, J. G. *J. Am. Chem. Soc.* **1967,** *89,* 1790.