Photochemistry of Ketone Polymers. I. Studies of Ethylene–Carbon Monoxide Copolymers

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ABSTRACT: The photolysis of copolymers of ethylene and carbon monoxide containing 1–9 mol % CO has been studied in solution and in the solid phase. Irradiation of the copolymer with light of wavelength 3130 Å results in molecular weight degradation, evolution of carbon monoxide, and the formation of terminal vinyl groups. These effects are explained in terms of the well-known Norrish type I and type II reactions of ketones. The type II reaction, an intramolecular elimination, appears to be independent of temperature and phase and is not quenched by atmospheric oxygen. In the glass transition region, however, the type II reaction is inhibited, probably due to restriction of the freedom of internal motion of the polymer chain. The type I reaction produces free radicals and is temperature dependent. At 120°, the two processes make approximately equal contributions to a total quantum yield for reaction of about 0.05. However, at ambient temperature the type II process accounts for the major part of the chemical reaction.

One of the main factors contributing to the weathering of polymeric materials is the degradation caused by the absorption of ultraviolet light. This study was initiated in the hope that it would provide some insight into the mechanisms of such degradation, by indicating the way in which a polymeric environment would influence the photochemistry of a system.

The photolysis of copolymers of ethylene and carbon monoxide was studied under a variety of conditions. This particular system possesses a number of advantages. First, at low carbon monoxide concentrations, the physical properties of the copolymer are almost indistinguishable from those of low density polyethylene. Second, the carbonyl group is one which is most likely to be formed in polymers degraded in an oxygen atmosphere, and is believed to play a large part in the determination of polymeric materials. Third, the photolysis of low molecular weight ketones has been the object of a great deal of practical and theoretical study in recent years, with the result that there exists a solid background of experimental data for comparison with that for polymeric systems.

The ketone group has a typical n–π^* transition which results in an appreciable absorption in the near-ultraviolet region and so is suitable for photochemical studies at wavelengths emitted by the sun and transmitted by the earth's atmosphere (*i.e.*, $\lambda > 3000$ Å). This is not true of most other chromophores found in synthetic polymers, such as ester, amide, nitrile, etc. In Figure 1 are compared the absorption spectra of an ethylene–carbon monoxide copolymer, containing 1% CO, and a typical long chain symmetrical ketone (12-tricosanone). The spectra are sufficiently similar to suggest that the absorption process is the same in both cases. If this is true, the problem remains to determine whether any difference exists, between the polymer and ketone, in the modes of dissipation of the excitation energy.

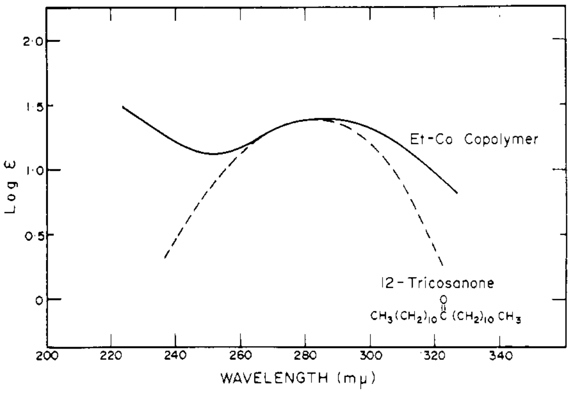

Figure 1. Comparison of the ultraviolet absorption spectra of a 1% ethylene–carbon monoxide copolymer, and 12-tricosanone; ϵ = molar decadic extinction coefficient. Polymer spectrum measured in *n*-heptane at 90°; concentration = 100 g/l. Ketone spectrum measured in 2-methylheptane at 25°; concentration = 10 g/l.

We can distinguish between photophysical and photochemical routes for this energy dissipation. The photophysical processes comprise fluorescence, phosphorescence, energy transfer, and radiationless conversion into thermal energy. The photochemical processes can result in photoionization, free radical formation, cyclization, or intramolecular rearrangement. Studies of the photochemical reactions can lead to some insight into the relative importance of both the physical and chemical processes.

On photolysis, all aliphatic ketones dissociate to some extent by the Norrish type I free-radical process.

$$\begin{array}{l} R_1COR_2 \xrightarrow{h\nu} R_1CO\cdot + \cdot R_2 \\ \qquad\qquad\searrow \; R_1\cdot + COR_2 \end{array}$$

The more complex ketones can also undergo an intramolecular rearrangement, the Norrish type II process,[1] to yield an olefin and a methyl ketone. For

$$R_1\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_2CHR_2R_3 \xrightarrow{h\nu} R_1\overset{\overset{\displaystyle O}{\|}}{C}CH_3 + CH_2{=}CR_2R_3$$

the type II reaction to occur, the ketone must possess a hydrogen atom on the carbon atom which is in the γ position with respect to the carbonyl group. There is

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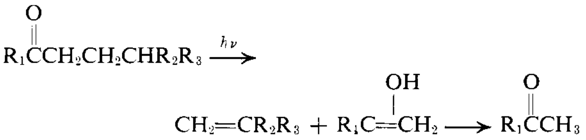
(1) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1504 (1935).

evidence which suggests that the type II reaction proceeds by intramolecular hydrogen transfer, to yield an enol, which then rearranges to the final ketone.[2,3]



$$R_1\overset{O}{\overset{\|}{C}}CH_2CH_2CHR_2R_3 \xrightarrow{h\nu} CH_2{=}CR_2R_3 + R_1\overset{OH}{\overset{|}{C}}{=}CH_2 \longrightarrow R_1\overset{O}{\overset{\|}{C}}CH_3$$

The hydrogen transfer proceeds *via* a six-membered cyclic intermediate,[4,5] in either a concerted or a stepwise process.

Although it has been shown by Wagner and Hammond that the type I and type II processes involve both the singlet and triplet excited states of the ketone,[6] the resolution of the individual contributions of these states is still a field of continuing intensive investigation.[7]

A third primary process has also been observed by Yang and Yang in ketone photolysis,[8] which results in the formation of a cyclobutanol derivative. This reaction, however, has only been identified in a few of the ketones studied.

Guillet and Norrish showed that the type I and type II reactions occur in polymeric systems, and the photolytic degradation of poly(methyl vinyl ketone) was explained in terms of these processes.[9] This conclusion was later confirmed by Wissbrun.[10] In addition the type II reaction has also been observed in polyesters, such as poly(ethylene terephthalate),[11] and in poly(*t*-butyl acrylate),[12] and it may be a major cause of degradation in a wide variety of synthetic polymers containing ester or ketone carbonyl groups.

Experimental Section

Apparatus. The 3130-Å line of the mercury emission spectrum was used as a source of light, 1 einstein of light of this wavelength having energy equivalent to 91.4 kcal which is not enough to break the C=O bond, but more than enough to break the C–C single bond. To supply the light energy, two lamps were used. One was a 1-kW high pressure (110 atm) water cooled mercury arc, Type AH-6 (General Electric). The other was a 250-W, medium pressure (30 atm) compact source mercury arc, Type ME/D (Associated Electrical Industries Ltd.). The 3130-Å line was isolated by means of a sheet of Pyrex plate glass and 2 cm of filter solution (115 g of $NiSO_4 \cdot 6H_2O$ + 35 g of $CoSO_4 \cdot 7H_2O$ in 250 ml of H_2O). Analysis of the light from the ME/D lamp filtered by this system showed a main peak at 3130 Å, with smaller peaks at 3040 Å, and 3360 Å. The analysis was carried out using a Jarrell-Ash 82-410 grating monochromator, 25-μ slits, a 1P28 photomultiplier tube, and a Hewlett-Packard 425-Å vacuum-tube microvoltmeter. The light intensity from the lamp was monitored by means of a 1P28 photomultiplier tube, powered by a Lambda Model 25 regulated power supply; the signal from the phototube was measured on a Leeds and Northrup Model G recorder. The intensity of the light was measured, and the photomultiplier tube calibrated using uranyl oxalate actinometry. Light entering the photomultiplier tube was further filtered by a Corning 9863 filter and a neutral density filter. The response from the photomultiplier tube was linear over the whole range of intensities measured (0–8.5 × 10^{-4} einstein/hr). For calibration purposes, blackened copper screens were used as neutral density filters.

The light from the lamp was focused by a quartz lens into a parallel beam, which passed successively through a filter cell, a bath containing the reaction cell, and into the photomultiplier tube. The filter cell, the reaction cell, and the windows of the bath were all made of fused quartz. The lens, bath, and photomultiplier tube housing were all rigidly mounted on an optical bench. Temperature control inside the bath was achieved by using either a circulating water pump (±0.25°) or a hot air blower (±1°).

Procedure. For photolysis of the ethylene–carbon monoxide copolymer in solution, the AH-6 lamp and a 20-mm path length quartz cell were used. The cell was filled with the solvent, pure *n*-heptane, and the intensity of the lamp measured, at the temperature of the experiment. Freeze-dried polymer was then added to make a 2% solution, which absorbed about 25% of the light. The polymer was dissolved, and the solutions were mixed by a stream of dry nitrogen, which also served to flush out any air dissolved in the solvent. The light beam was then allowed to enter the cell and the photolysis commenced, the intensity of the emergent beam being monitored by the photomultiplier tube and the recorder. At the end of the photolysis the cell was filled with pure solvent and the intensity of the lamp measured again. The polymer was recovered from the solution by evaporation of the heptane, dissolved in benzene, and freeze-dried. Some photolyses were also done using a Pyrex cell of 60 mm path length, and the unfiltered light of the ME/D lamp.

The 1% ethylene–carbon monoxide copolymer was also irradiated in the solid phase in the form of a thin film. Compression-molded films were fixed on plates which fitted into a Perkin-Elmer 521 infrared spectrophotometer. An infrared spectrum of the polymer could thus be obtained after each period of photolysis without disturbing the film. For photolyses at room temperature and above, the plates were mounted in a solid brass cell through which a stream of inert gas could be passed while the cell was being heated by hot air.

For photolyses below room temperature a cell was constructed from polystyrene foam. The interior of the cell was cooled by a flow of nitrogen which had passed through a coil immersed in liquid nitrogen, the temperature being controlled by the rate of flow of gas. The temperature inside the cell was measured by means of an iron–constantan thermocouple and a vacuum-tube voltmeter.

To determine the amount of light absorbed by the films, the ultraviolet spectrum of each one was run before photolysis. To correct for scattering, a piece of film of the same thickness as the polymer was placed in the reference beam of the spectrophotometer. This film was made from the same type of polyethylene, but contained no carbonyl groups.

Analysis. The number average molecular weight of the degraded polymer was measured on an ebulliometer, using toluene as a solvent, and a tristearin standard. Infrared spectra of the polymer, both before and after photolysis, were run on a Perkin-Elmer 521 double beam grating spectrophotometer, using compression-molded films. Film thicknesses were determined by means of a micrometer.

Carbon monoxide, a product of the polymer photolysis,

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(2) G. R. McMillan, J. G. Calvert, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **86**, 3602 (1964).

(3) R. Srinivasan, *ibid.*, **81**, 5061 (1959).

(4) F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938).

(5) W. Davis, Jr., and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **60**, 2153 (1947).

(6) P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

(7) C. H. Nicol and J. G. Calvert, *ibid.*, **89**, 1790 (1967).

(8) N. C. Yang, and D. D. H. Yang, *ibid.*, **80**, 2913 (1958).

(9) J. E. Guillet and R. G. W. Norrish, *Proc. Roy. Soc.* (London), **A233**, 153 (1955).

(10) K. F. Wissbrun, *J. Amer. Chem. Soc.*, **81**, 58 (1959).

(11) K. R. Osborn, *Amer. Chem. Soc., Div. Org. Coatings Preprints*, **21** (2), 411 (1961).

(12) A. R. Monahan, *J. Polym. Sci., Part A-1*, **4**, 2381 (1966); 2333 (1967).

was collected and measured on a gas chromatograph, in a separate series of experiments. The polymer solution was flushed with hydrogen, before, during, and after photolysis, sweeping any evolved gases through activated charcoal cooled in liquid nitrogen. The tube containing the charcoal was then closed, most of the hydrogen pumped off, at liquid nitrogen temperature, and connected to the gas chromatograph. After the tube had been allowed to warm up to room temperature, any desorbed gases were swept into the gas chromatograph by a stream of hydrogen (carrier gas) where they were separated by a 5-Å molecular sieve column using a thermal conductivity detector. The peak areas were compared with the peak areas of known volumes injected before and after the collected sample.

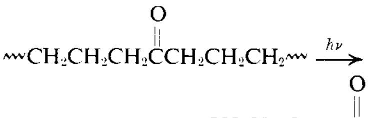
Materials. The polymer used in most of the experiments described in this paper was a copolymer of ethylene and carbon monoxide, containing 1% by weight carbon monoxide, polymerized by a high-pressure process. The polymer was a research sample supplied by the Tennessee Eastman Co., and to render it more easily soluble it was freeze-dried from benzene solution before use.

The solvents used in the photolyses were purified by distillation, and filtered through silica gel columns until they were completely transparent over the whole range of wavelengths passed by the filter system. A Perkin-Elmer Model 800 gas chromatograph was used for analysis, with flame ionization detectors and $^1/_8$ in. × 5 ft columns, 5% w/w silicone SE 30 on Chromosorb G. Ultraviolet spectra were run on a Bausch and Lomb Spectronic 505 double beam spectrophotometer. Viscosities of the solvents were measured using a Desreux viscometer.

Results and Discussion

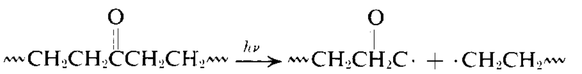
Absorption of light in the near-ultraviolet region by the ethylene–carbon monoxide copolymer results in a decrease in molecular weight, accompanied by the evolution of carbon monoxide. In addition the infrared spectrum of the degraded polymer shows an increase in the absorbance at 11.0 μ, characteristic of the terminal vinyl double bond $\mathrm{RCH{=}CH_2}$.

These results are consistent with a mechanism for the degradation of the copolymer based on the type I and type II reactions. The type II reaction produces a methyl ketone and a terminal vinyl group (eq 1)



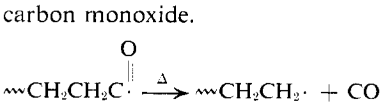
$$\sim\mathrm{CH_2CH_2CH_2}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_2CH_2CH_2}\sim \xrightarrow{h\nu} \sim\mathrm{CH_2CH_2CH_2}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_3} + \mathrm{CH_2{=}CH}\sim \tag{1}$$

while the type I reaction produces two polymer radicals



$$\sim\mathrm{CH_2CH_2}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_2CH_2}\sim \xrightarrow{h\nu} \sim\mathrm{CH_2CH_2}\overset{\overset{\mathrm{O}}{|}}{\mathrm{C}}\cdot + \cdot\mathrm{CH_2CH_2}\sim \tag{2}$$

(eq 2). Both reactions therefore bring about scission of the polymer chain, and in addition, at elevated temperatures the acyl radical produced in the type I reaction can subsequently decarbonylate with the evolution of carbon monoxide.



$$\sim\mathrm{CH_2CH_2}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\cdot \xrightarrow{\Delta} \sim\mathrm{CH_2CH_2}\cdot + \mathrm{CO}$$

If $(\overline{M}_n)_0$ is the number average molecular weight of the starting material, and $\overline{M}_n$ is the number average molecular weight of the degraded polymer, then $((\overline{M}_n)_0/\overline{M}_n) - 1$ is equal to the average number of polymer bonds broken per original polymer molecule. This quantity is shown in Figure 2, for photolysis of the polymer in hydrocarbon solution, plotted as a function of the light absorbed. It can be seen that the rate of bond breaking is initially linear, but slows down as the reaction proceeds. From the initial slope of the curve, the quantum yield for bond breaking was calculated to be 0.040 ± 0.004 in *n*-heptane solution, at 90°.

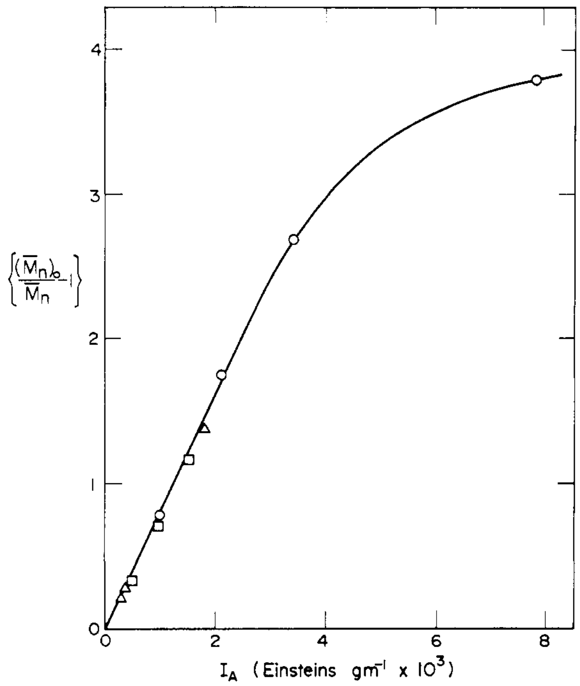


Figure 2. Number of bonds broken as a function of the light absorbed per gram of polymer (I_A) during photolysis of 1% ethylene–carbon monoxide copolymer in *n*-heptane solution at 90°; polymer concentration = 25 g/l.; $(M_n)_0$ = 18,900: ⊙, Pyrex cell, unfiltered mercury arc, absorbed intensity, = 3 × 10^{-7} einstein/g sec; ⊡, quartz cell, filtered mercury arc, absorbed intensity = 8 × 10^{-8} einstein/g sec; ◬, quartz cell, filtered mercury arc, absorbed intensity = 10^{-8} einstein/g sec.

One reason for the observed decrease in the rate of degradation of the copolymer is readily apparent when it is remembered that one of the type II reaction products is a polymer chain which terminates in a $\mathrm{-C({=}O)-CH_3}$ group. The concentration of these groups increases as the photolysis proceeds, and although they continue to absorb light, reaction of these groups by either type I or type II would produce no detectable change in the molecular weight.

The infrared absorbence of the degraded polymers at 11.0 μ, characteristic of vinyl double bonds, is expressed as the absorptivity, K, per centimeter path length, for a concentration of 1 g/ml of the polymer according to the equation

$$K = \frac{1}{dl}\log\frac{I_0}{I}$$

where d is the density of the polymer, l the path length, and $\log(I_0/I)$ is the absorbance at 11.0 μ after correction for background absorption. Figure 3 shows the increase in absorbtivity at 11.0 μ, ΔK, for the 1% ethylene–carbon monoxide copolymer, as the photolysis proceeds. Using the initial rate and 1-decene as a

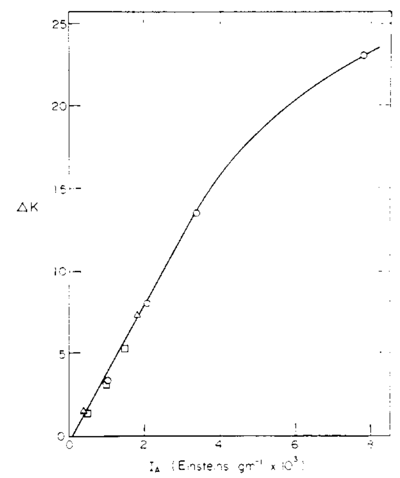


Figure 3. Increase in absorptivity (ΔK) at 11.0 μ as a function of light absorbed per gram of polymer (I_A) during photolysis of a 1% ethylene–carbon monoxide copolymer in *n*-heptane solution at 90°; polymer concentration = 25 g/l: ⊙, Pyrex cell, unfiltered mercury arc, absorbed intensity = 3×10^{-7} einstein/g sec; ⊡, quartz cell, filtered mercury arc, absorbed intensity = 8×10^{-8} einstein/g sec; △, quartz cell, filtered mercury arc, absorbed intensity = 10^{-8} einstein/g sec.

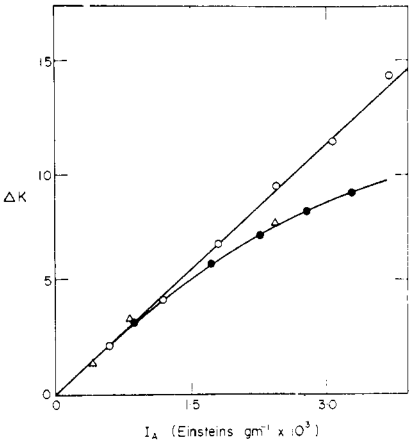


Figure 4. Increase in absorptivity (ΔK) as a function of light absorbed per gram of polymer during photolysis of a 1% ethylene–carbon monoxide copolymer in the solid phase: film thickness = 0.018 cm; absorbed intensity = 7.6×10^{-8} einstein/g sec; ⊙, photolysis in air at 24°; ●, photolysis in nitrogen at 90°; △, photolysis in air at 90°.

standard with which to calibrate the absorbance, the quantum yield for vinyl double bond production was calculated to be 0.025 ± 0.003 in *n*-heptane solution, at 80°.

As with the rate of bond breaking, the rate of vinyl double bond production slows down in the later stages of the photolysis, possibly due to removal of the double bonds by radicals produced in the type I reaction

$$R\cdot + {\sim\!\sim}CH_2CH{=}CH_2 \longrightarrow {\sim\!\sim}\dot{C}HCH_2R$$

where R · could be a polymer radical, but in the presence of a large amount of hydrocarbon solvent it would be more likely to be a radical produced by the abstraction of a hydrogen atom from a solvent molecule.

$${\sim\!\sim}CH_2CH_2\cdot + SH \longrightarrow {\sim\!\sim}CH_2CH_3 + S\cdot$$

Photolysis of the ethylene–carbon monoxide copolymer in the solid phase produced the results shown in Figure 4, where the increase in absorptivity, ΔK, at 11.0 μ has again been plotted as a function of light absorption.

It was observed that the polymer exhibited the same initial rate of vinyl double bond production at 90 and 24°, in both the presence and absence of oxygen; furthermore, the quantum yield calculated from this rate was the same value which was calculated for the polymer in solution at 90°, *i.e.*, 0.025 ± 0.003.

However, the plot of the increase in absorptivity at 24° remains linear for the duration of the photolysis, which can be contrasted with the eventual nonlinearity of the plot at 90°. Although it is generally accepted that the type II reaction occurs, at least in part, *via* the triplet state and that molecular oxygen is a triplet quencher, it is not surprising that oxygen does not have any apparent effect on the type II reaction in the 1% copolymer, for the following reasons.

If ϕ_0 and ϕ are the quantum yields for reaction, in the absence and presence, respectively, of a quencher Q, it can be shown that

$$\frac{\phi_0}{\phi} = 1 + \frac{k_q}{k_r + k_d}[Q]$$

where k_q, k_r, and k_d are the rate constants for the quenching of, reaction from, and deactivation of the triplet state, respectively.[13]

Assuming the quenching reaction to be diffusion controlled, we can substitute the diffusion constant for low density polyethylene at 90° [14] into theoretical equations for k_q[15] to obtain an approximate upper limit for k_q of $\sim 10^9$ l. mol⁻¹ sec⁻¹.

The solubility of oxygen in polyethylene is $\sim 10^{-3}$ *M*,[16] therefore, $k_q[O_2] \approx 10^6$.

In order that $(\phi_0/\phi) - 1$ should be $\geqslant 0.1$, *i.e.*, $\geqslant 10\%$ quenching, $k_r + k_d$ would have to be $\leqslant 10^7$. Experiments have shown, however,[17] that $k_r + k_d$ for the 1% Et–CO copolymer is at least 10^8 at 90°, so we would not expect to see the effects of oxygen quenching.

A possible explanation of the difference in shape of the plots at 90 and 24° is provided by the following kinetic scheme for the photolysis of the solid polymer, involving the removal of vinyl groups by radicals produced in the type I reaction, and the eventual removal of the radicals themselves by combination.

This would give rise to a steady-state concentration of radicals described by the equation

$$\frac{d[R]}{dI_A} = 2\phi_I - \frac{k_t}{I}[R]^2 = 0$$

where [R] = radical concentration (moles per gram of polymer); I_A = total light absorbed per gram of polymer; ϕ_I = type I quantum yield; I = rate of absorp-

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[13] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 93.

[14] A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, **50**, 413 (1961).

[15] J. Nafisi-Movaghar, J. B. Birks, and K. Razi Naqri, *Proc. Phys. Soc.* (London), **91**, 449 (1967).

[16] A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, **50**, 393 (1961).

[17] M. Heskins and J. E. Guillet, *Macromolcules*, **1**, 97 (1968).

tion of light (einstein/gram second); k_t = rate constant for termination of radicals (gram/mole second).

The original concentration of vinyl groups in the polymer is small, compared with the number produced by the type II reaction, allowing us to write

$$\text{vinyl double bond concentration} = Z\Delta K$$

where Z = calibration constant. Hence, the change in the infrared absorption of the film will be governed by the equation

$$\frac{Z\mathrm{d}\Delta K}{\mathrm{d}I_A} = \phi_{II} - \frac{k_p}{I}[\mathrm{R}]Z\Delta K$$

where k_p = the rate constant for the radical addition reaction

$$\mathrm{R}\cdot + {\sim}\mathrm{CH_2CH{=}CH_2} \longrightarrow {\sim}\mathrm{CH_2\dot{C}HCH_2R}$$

Substitution for [R] and integration yields the equation

$$\Delta K = \frac{\alpha}{\beta}\{1 - \exp(-\beta \cdot I_A)\}$$

where $\alpha = \phi_{II}/Z$

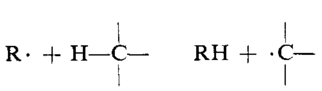
$$\beta = \left(\frac{k_p^2}{k_t} \cdot \frac{2\phi_I}{I}\right)^{1/2}$$

For the photolysis at 90°, a fit to the curve is given by

$$\Delta K = 16.13[1 - \exp(-250 I_A)]$$

which gives a value for $k_p/\sqrt{k_t} = 0.013$ ($\mathrm{l.^{1/2}\ mol^{-1/2}\ sec^{-1/2}}$) in a comparison with a value of 0.01 for the same ratio in ethylene polymerization at 80°.[18]

A possible mechanism for the rapid diffusion of radicals in the solid polymer is by intermolecular hydrogen abstraction



$$\mathrm{R}\cdot + \mathrm{H{-}\overset{|}{\underset{|}{C}}{-}} \qquad \mathrm{RH} + \cdot\mathrm{\overset{|}{\underset{|}{C}}{-}}$$

This reaction has been proposed to explain some of the effects in the radiolysis of solid polyethylene.

If diffusion was by this process, k_t would have an activation energy of ~10 kcal/mol and k_p would have an activation of ~14 kcal/mol, 10 kcal for the diffusion process and ~4 kcal for the addition reaction. (As will be seen later, ϕ_I has an activation energy of about 5 kcal/mol).

Using these activation energies to calculate $k_p/\sqrt{k_t}$ and ϕ_I at 24°, the dependence of ΔK on I_A at the lower temperature is given by

$$\Delta K = 735[(1 - \exp(-5.26 I_A))]$$

which is the same as is obtained by experiment. It is apparent, however, that any value of β, if sufficiently small, would result in ΔK becoming a linear function of I_A with gradient α. Additional support for the above diffusion process is provided by the fact that the polymer film irradiated at 90° showed an increased infrared absorption at 10.4 μ. This could possibly be due to the production of internal double bonds of the type *trans*-RCH=CHR′. These might be expected to result from disproportionation of secondary polymer radicals.

Table I shows the quantum yield for vinyl group formation in the 1% Et–CO copolymer, at various temperatures down to −150°. Between 90 and −25° the quantum yield is independent of temperature, and at 90° it is also the same as in dilute solution.

TABLE I
PHOTOLYSIS OF 1% ET–CO COPOLYMERS IN THE SOLID PHASE

Temp, °C	Quantum yield for vinyl group formation (ϕ_{II})
90	0.025
24	0.025
−25	0.025
−50	0.015
−68	0.013
−95	0.005
−150	0.000

Clearly the quantum yield for vinyl group formation at these temperatures is not affected by large changes in the over-all mobility of the polymer molecules. This phenomenon has been observed previously in other carbonyl-containing polymers.[9–11]

Between −25 and −50°, however, the quantum yield begins to decrease with temperature, and at −150°, there is no observable formation of vinyl groups when a film of the copolymer is photolyzed. It is interesting to view this behavior in the light of present knowledge of both the type II reaction and molecular motion in polyethylene.

Polyethylene undergoes a second-order transition at about −30°.[19] This has been interpreted by Wunderlich[20] as the first phase of an abnormally long glass transition region in polyethylene, due to a freezing-in of hole equilibrium. As a result of this transition, the hitherto free rotation about C–C bonds changes to a hindered, cooperative motion of at least three carbon atoms. The glass transition region ends at about −120°, and at this temperature even the cooperative, or "crankshaft," rotation is frozen in, and no motion other than vibration is found in the polymer.

This picture of the molecular motion in polyethylene in the glass transition region is supported by nuclear magnetic resonance measurements. In the nmr absorption spectrum of branched polyethylene, a narrow component is observed at about −120°, ascribed to liquidlike motion of the polymer chains. As the temperature rises the intensity of this narrow component increases, but the width of the line decreases.[21]

A plot of the correlation frequency for the motion responsible for line narrowing is made up of two distinct parts. The high-temperature region, above about −35°, in which the activation energy for motional narrowing is 8 kcal/mol, and the low-temperature region, below −35°, in which the activation energy is ~2 kcal/mol. The line narrowing in the high-temperature region has been ascribed to large amplitude rotational and translational motion, while in the low-temperature region it has been attributed to rotation or rotational oscillation of small amplitude.

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[18] "Polymer Handbook," John Wiley and Sons, Inc., 1966, p II-59.

[19] R. F. Boyer, *Rubber Chem. Technol.*, **36**, 1303 (1963).

[20] B. Wunderlich, *J. Chem. Phys.*, **37**, 2429 (1962).

[21] D. W. McCall and W. P. Slichter, *J. Polym. Sci.*, **26**, 171 (1957).

TABLE II

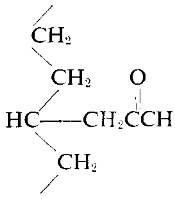
Polymer	Solvent	Temp, °C	Solvent viscosity	ϕ_{CO}
1% Et–CO	Heptane	90	0.22	0.012 ± 0.002
1% Et–CO	Decane	90	0.4	0.012 ± 0.002
1% Et–CO	Paraffin oil	120	2.1	0.021 ± 0.002
1% Et–CO	Dodecane	120	0.4	0.022 ± 0.002
0.5% Et–CO	Paraffin oil	120	2.1	0.020 ± 0.002
3.5% Et–CO[a]	Paraffin oil	120	2.1	0.020 ± 0.002
9.1% Et–CO[b]	Paraffin oil	120	2.1	0.035 ± 0.002

[a] High molecular weight not completely soluble (M.I. (Melt Index) = 0.67). [b] Low molecular weight (M.I. = 9000).

Since the 1% Et–CO copolymer is physically indistinguishable from high-pressure polyethylene, we would therefore expect rotation of the polymer chains to become hindered at about −35°. Also, if the type II reaction does in fact proceed *via* a six-membered cyclic transition state, the formation of this configuration in the copolymer would be rendered more difficult at this temperature, with the result that the quantum yield would decrease, eventually disappearing at about −120°.

Moreover, although the number of determinations is too small for a rigorous analysis, the activation energy for the decrease in quantum yield is approximately 2 kcal/mol. Thus the evidence indicates that the diminution in quantum yield below −35° is caused by the same factors which lead to broadening of the nmr absorption line, namely, hindrance of rotation about C–C bonds. Above −35°, since there is no restriction to rotation about C–C bonds, the type II quantum yield would not be expected to show any marked temperature dependence.

Table II shows the quantum yields obtained for carbon monoxide evolution (ϕ_{CO}) from solutions of some Et–CO copolymers. The value of ϕ_{CO} for the 1% Et–CO copolymer at 120° in paraffin oil (0.021) is significantly higher than the extrapolated value obtained (0.012) from photolyses of long-chain symmetrical aliphatic ketones,[22] also in paraffin oil at 120°. This is possibly due to the existence of short chain, carbonyl-containing branches in the copolymers, *e.g.*



Carbonyl groups in such branches would be expected to have a higher ϕ_{CO}, compared with carbonyl groups in the chain backbone. Some support for this hypothesis is provided by the fact that a 9.1% Et–CO copolymer, photolyzed under the same conditions has an even higher ϕ_{CO} (0.035). However, since the 9.1% Et–CO copolymer has a lower number average molecular weight than the 1% Et–CO copolymer, it will contain a larger number of carbonyl groups situated close to chain ends, and these may also possess high CO quantum yields.

Further reference to Table II reveals that ϕ_{CO} for the 1% Et–CO copolymer shows little dependence on solvent viscosity; indeed ϕ_{CO} for the undiluted copolymer at 120° is 0.018. However, ϕ_{CO} does increase with temperature, with an activation energy (90–120°) of about 5 kcal/mol. At 25°, an activation energy of this magnitude would reduce ϕ_{CO} to 2–3 $\times 10^{-3}$, or about 10% of ϕ_{II}.

This type of behavior was observed in aliphatic ketones of moderate chain length,[22] and is perhaps produced by a modified form of the "cage" effect.[23,24] This would reduce the mobility of segments of the polymer chain in the immediate vicinity of the carbonyl group. On photolysis, therefore, the most probable reaction for the radicals produced by the photolysis is immediate recombination, resulting in a low CO quantum efficiency.

If the solvent molecules are long enough, only a part of any one molecule would be involved in forming any cage, and the effect produced would be independent of the total length of the solvent chain.

In conclusion it appears that ethylene–carbon monoxide copolymers degrade photolytically by the classic Norrish type I and II reactions of ketones. At ordinary temperatures the type II reaction predominates and is the major cause of chain breaking. The reaction seems to be unaffected by the mobility of the polymer molecules but does depend on the freedom of internal motion of the chain. Although it is believed that a substantial portion of the reaction proceeds *via* the triplet n–π* intermediate, no quenching by atmospheric oxygen is observed, probably because of the relatively low equilibrium concentration of oxygen in the polymer.

The type I reaction, which involves free radical intermediates, is strongly temperature dependent. At 25° it accounts for only about 10% of the total reaction, but at 120° it has a quantum efficiency about the same as type II. At this temperature the total quantum yield for chemical reaction is about 0.05, the remainder of the energy (95% of the total energy absorbed) being dissipated as heat, probably by nonradiative transitions from the excited singlet and triplet.

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