two different masses existed. For example, numbering the plateaus from 1 to 6 beginning at the top, the voltage of the break between plateaus 4 and 5, 620 V, is almost exactly twice that between plateaus 2 and 3, 317 V, etc. It must be pointed out, however, that this work is just beginning and we have not yet learned how to control the electrospray so as always to obtain plateaus of the type of Figure 1. Nevertheless, the plateaus have been obtained in a number of experiments and we believe them to be real. Incidentally, the existence of the plateaus demonstrates a high degree of velocity monochromatization[5] which should be especially significant in the case of macroions as a component of the gas stream. The possibility that some of the ions consisted of aggregates of macromolecules or of macromolecules with condensed solvent molecules cannot be excluded. Thus, the drop in current from plateau 1 to 2 might be due to repelling ions of mol wt 51,000 with a single unit charge (calculations indicate that this is about the correct repeller voltage) and the drop from 2 to 3 to repelling ions of a double aggregate of molecular weight twice 51,000 with a single unit charge. It is planned to build a time-of-flight mass spectrometer to measure mass-to-charge ratios and so to enable us to make a more quantitative study of the macroions produced by the electrospray technique.

Acknowledgment. This research was supported by a grant to Northwestern University by the National Institute of General Medical Sciencies, Grant No. GM13194. We are indebted to Dr. K. Katsuura for some early studies of our plans for the macromass spectrometer during his tenure of a Postdoctoral Fellowship at Northwestern University during the academic year 1963–1964. The work at Bendix was done under a subcontract with Northwestern University. We are much indebted to C. H. Tosswill, Head of the Advanced Instrumentation Department, Bendix Research Laboratories, for his helpful interest in and support of this research. Subsidiary aid from the Advanced Research Projects Agency through the Northwestern University Materials Research Center is also gratefully acknowledged.

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Received October 13, 1967

Mechanism of Ultraviolet Stabilization of Polymers

The weathering degradation of polymers in outdoor applications can often be attributed to photochemical reactions initiated by the absorption of light by a carbonyl group in the polymer. In the case of polyethylene, for example, such groups have seen shown to be formed by air oxidation during the molding or extrusion process.

To protect polymers from weathering degradation, it has become common practice to compound them with a uv stabilizer such as a substituted hydroxybenzophenone which absorbs most of the ultraviolet radiation and dissipates the energy in a harmless manner. Such a stabilizer behaves essentially as an ultraviolet screen. Recently, it has been suggested[1] that stabilization of polymers is also possible by a mechanism which involves a direct transfer of the electronic energy from the excited state of the polymer molecule to a suitable stabilizer molecule. We wish to report experimental evidence that such a process can indeed take place and may represent an important stabilizing mechanism for polymeric systems.

It has been shown by Hartley and Guillet[2] that ethylene–carbon monoxide copolymers which contain ketone groups in the main chain undergo the same photochemical reactions as simple aliphatic ketones and may be used as model systems for studying photodegradation. The main reactions are the Norrish type I (eq 1) and type II

$$\sim\!CH_2CH_2\overset{\overset{O}{\|}}{C}CH_2CH_2\sim \longrightarrow \sim\!CH_2CH_2\overset{\overset{O}{\|}}{C}\cdot + \cdot CH_2CH_2\sim \quad \text{or } \sim\!CH_2CH_2\cdot + \cdot CH_2CH_2\sim + CO \qquad (1)$$

(eq 2). Both these processes break the chain and the

$$\sim\!CH_2CH_2\overset{\overset{O}{\|}}{C}CH_2CH_2\sim \longrightarrow \sim\!CH_2COCH_3 + CH_2{=}CH\sim \qquad (2)$$

net effect can be determined by following the rate of change in the molecular weight of the polymer. In the present experiments the quantum yield for the degradation of the polymer was determined in solutions of decahydronaphthalene at 80° in the presence of varying amounts of 1,3-cyclooctadiene (COD). This compound has been shown to be an efficient acceptor of triplet excitation energy from acetophenone[3] which has a triplet energy similar to that of the aliphatic ketones.[4] The irradiations were carried out in a thermostated quartz cell using light of 3130 Å from a medium-pressure mercury arc, isolated by means of a Jena uv P.I.L. interference filter. The light absorbed was monitored by a photomultiplier which was calibrated by uranyl oxalate actinometry. The solutions were degassed by several freeze–thaw cycles under high vacuum and sealed under vacuum. The molecular weights were determined by single-point viscosity measurements in a viscometer sealed to the reaction cell. The limiting viscosity number $[\eta]$ was calculated from the logarithmic viscosity number using the value of k in the equation

$$\frac{\ln \eta_r}{c} = [\eta] - k[\eta]^2 c$$

determined in a separate set of experiments. The relation used for molecular weights was $[\eta] = 3.873 \times 10^{-4} \bar{M}_n^{0.738}$ as determined by Uberreiter, *et al.*[5] The

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TABLE I
QUANTUM YIELD OF CHAIN BREAKING IN ETHYLENE–CO COPOLYMERS

Concentration of COD, mol/l.	ϕ, mol/einstein
0.000	0.0505
0.038	0.0430
0.079	0.0355
0.092	0.0350
0.122	0.0326
0.207	0.0281
0.387	0.0283
0.410	0.0270

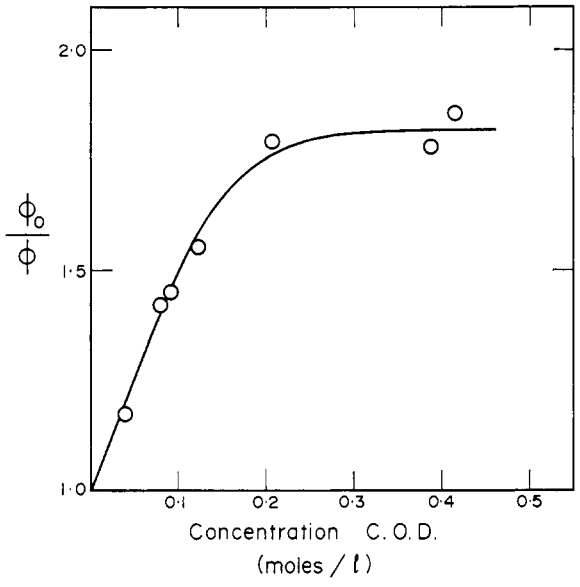

Figure 1.

quantum yield for chain breaking (ϕ) was determined from the initial slope of the line obtained by plotting $[(\bar{M}_n)_0/\bar{M}_n] - 1$ as a function of the light absorbed by the system. The results of experiments using a 1.8% solution (6×10^{-3} mol/l. of CO) are shown in Table I. Under the conditions of the experiment (at 3130 Å), all the light is absorbed by the polymer and none by the COD. We attribute the reduction in the quantum efficiency to the quenching of the triplet (n–π^*) state of the ketone by transfer of the electronic energy to the COD. Such a process has been shown to occur in simple aliphatic ketones in solution by Wagner and Hammond[6,7] and by Dougherty[8] using piperylene as the acceptor.

Figure 1 shows a plot of ϕ_0/ϕ against the concentration of COD. Since the decrease in molecular weight is due to both type I and type II processes, it is not expected that a simple linear Stern–Volmer relationship will be observed. However, studies of quenching in simple ketones[6,7] show a similar effect, which has been ascribed to the fact that some of the type II reaction arises from the excited singlet state and is not quenched. Complete quenching of all reaction is therefore not possible and ϕ will remain at a finite value independent of the concentration of quencher after a certain concentration has been reached.

The initial slope of this curve is equal to $k_q/\Sigma k_r$, where k_q is the bimolecular rate constant for quenching and Σk_r is the sum of the rate constants for all the reactions quenched. From these experiments we do not have sufficient information to evaluate the magnitude of the individual rate constants, but from the maximum quenching observed we can estimate that about 45% of the total reaction involves the triplet state of the carbonyl group. This is somewhat less than that observed with the lower aliphatic ketones at 30° (65%). (The latter figure however refers to type II products only.)

This mechanism of energy transfer is evidently not particularly effective in the present example, since only a 45% reduction in the rate of degradation can be obtained even with quite high stabilizer concentrations. However, it may well be possible to find additives which will quench both the singlet and triplet states, in which case more effective stabilizing action could be expected. It may well be that the effectiveness of carbon black as a weathering stabilizer is related to its ability to accept electronic excitation energy directly from the polymer molecule. The conjugated double bonds present in most forms of carbon black are not unlike those in COD and the structural variations would ensure that almost any desired energy levels would be available for quenching.

Acknowledgments. The authors wish to acknowledge the financial support of the National Research Council of Canada and a fellowship (M. H.) from the Xerox Corporation.

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A Mechanism for the Oxidative Photodegradation of Polyethylene

Several studies of the fundamental processes occurring in the oxidative photodegradation of polyethylene have been reported.[1] While the later stages of the photooxidation evidently involve radical chains similar to those of thermal oxidation, the primary stages are less clearly understood. This paper proposes a new mechanism for the oxidative photodegradation of polyethylene and presents experimental evidence supporting it. The mechanism is consistent with (1) known photochemistry of model systems resembling polyethylene and with (2) known products of polyethylene photooxidation. In addition, the formation and role of *electronically excited* oxygen molecules in the photodegradation is described.

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