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Photostabilization of Polypropylene. III. Stabilizers and Macro Ketones[1,2]

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ABSTRACT: The effects of some polypropylene photostabilizers on the photolysis of macro-ketonic products have been investigated for irradiation under vacuum or air in polypropylene films. A nickel chelate was found to inhibit the formation of Norrish type I and II products from the macro ketones. Various stabilizers retarded polypropylene photooxidation sensitized by the macro ketones. The stabilizers probably operate *via* a collisional quenching process and radical scavenging rather than by long-range energy transfer. Quenching of the macro-ketone phosphorescence at 77°K was not detected with any of the investigated stabilizers.

The quenching of ultraviolet (uv) excited macro-carbonyl impurities has often been invoked[3-5] as the prime mode of photostabilization of polypropylene (PP) and polyethylenes. Usually a Förster type of long-range energy transfer has been assumed especially for certain uv stabilizers of the metal chelate type, although the interpretation of the data of Chien and Conner[6] which supports this assumption has been questioned.[7,8] In fact recent work on model systems now indicates that ketone quenching by metal chelates occurs by a collisional process, at or below the diffusion-controlled rate in the liquid phase.[7-9] Nevertheless, the interaction of uv stabilizers in PP articles with macro ketones akin to those expected to be formed in PP under processing conditions[10] is still of fundamental and applied interest.[11]

In this paper, we present some limited data on the effects of a few common polyolefin uv stabilizers on both the photolysis of macro ketones in PP and on the photooxidation of PP containing these macro ketones.

Experimental Section

Materials. Isotactic PP resin powder (Moplen MF 20, Montecatini Edison) was briefly air-oxidized at 225°, and pressed into films (30–35 μ) as described previously.[10]

The stabilizers used included [2,2′-thiobis-4-(1,1,3,3-tetramethylbutyl)phenolato-*n*-butylaminenickel(II) (Ni-3), nickel bis[*o*-butyl(3,5-di-*tert*-butyl-4-hydroxybenzyl)]phosphonate (Ni-4), octadecyl 3-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)propionate (P-2), 2-hydroxy-4-dodecyloxybenzophenone (P-5), and 2,2′-thiobis(4-*tert*-octylphenol) (P-7). The abbreviations used are the same as those employed in our previous work.[2] Stabilizers were diffused into these films from isooctane solutions (2–5 wt % depending on solubility) at 25° for up to 20 days. These films were then briefly rinsed in the solvent, and vacuum dried for ~4 hr. Stabilizer concentrations were estimated from the uv absorptions of each film in comparison with isooctane solutions of the same stabilizer.

Film Spectra. Transmission ir spectra were recorded on a Beckman IR8 at 90 cm^{-1} min^{-1}. Uncorrected luminescence spectra were recorded on a Farrand Mk 1 spectrofluorometer equipped with a xenon source, an IP-28 photomultiplier, and a low-temperature attachment. Phosphorescence spectra were recorded by pulsing the spectrometer amplifier out of phase with the chopped incident illumination.[12]

Vacuum Photolysis. The radiation from a super pressure mercury lamp (Osram 500 W) was collimated and passed through 10 cm of water (ir filter) and a Corning CS 1-64 filter (λ >320 nm). Incident light intensities were measured by a thermopile.[10]

Films were irradiated under vacuum in 1-cm quartz cells, the volatile photolysis products collected and these products separated and identified by gas-phase chromatography using Poropak R and molecular sieve 5A columns, as described previously.[10]

Air Photolysis. Film samples were irradiated at 40° in an Atlas xenon arc Weather-Ometer (6000 W) with Pyrex inner and outer filters. These conditions approximate to noon summer sunlight.

Results and Discussion

Stabilizers were incorporated into the oxidized PP films by diffusion from solution rather than by dry blending prior to fusion so as to minimize stabilizer oxidative decomposition and to prevent any modification of the PP thermal oxidative process or the products from this oxidation by the stabilizers.

Photolysis Product Quenching. We have previously reported[10] that air oxidation of PP powder at 225° produces mainly macro ketones of the types $\sim CH_2C(=O)CH_2\sim$ (A) and $\sim CH_2C(=O)CH_3$ (B), with negligible hydroperoxides ($<5 \times 10^{-5}$ *M*). The photolysis of these macro-ketone-containing films (PP-ketone) *in vacuo* yields predominantly carbon monoxide (from the Norrish type I scission of A) and acetone (from the Norrish type II scission of B).[10] In the presence of Ni-3 (0.3 wt %), these same photolysis products were detected, although their rates of production were significantly reduced (Figure 1). Based on initial rates of product formation, the quantum yields in the presence and absence of Ni-3 were respectively 0.046 and 0.079 (acetone) and 0.030 and 0.067 mEinstein^{-1} (carbon monoxide). The absorbed light intensities used to calculate these values were corrected for the low inherent absorption of Ni-3 at >320 nm; the cited values are probably accurate to no better than

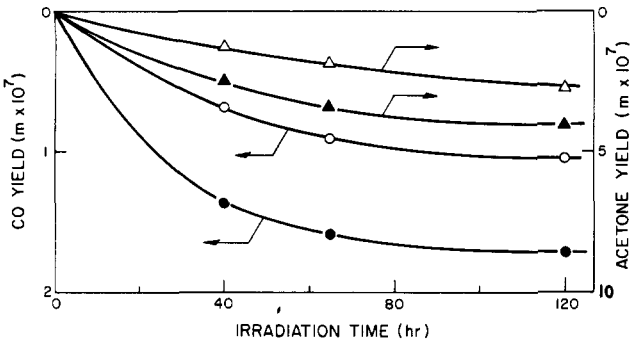


Figure 1. Vacuum photolysis of PP-ketone: product yields. Filtered Hg arc irradiation (λ >320 nm). Films 33 μ thickness, 0.02-g sample, 0.025 *M* in each of ketones A and B: (●,▲) stabilizer free; (○,△) with 0.30 wt % of Ni-3.

±15% due to analytical and photometric problems. The Ni-3 concentration did not decrease detectably up to 120-hr vacuum irradiation.

Vacuum irradiation of PP-ketone films produced a marked drop in the film >C=O ir absorptions at 1726 and 1718 cm^{-1}.[10] The ir changes observed in the presence and absence of Ni-3 are shown in Figure 2. Although the complex envelope of overlapping >C=O absorptions has not been resolved into its component peaks, it is obvious from Figure 2 that the rapid loss of the 1726- and 1718-cm^{-1} absorptions (largely due to ketones B and A, respectively[10]) has been significantly slowed by the presence of Ni-3. (The absorption at 1700 cm^{-1} is probably due to small amounts of strongly absorbing β-unsaturated carboxylic acids,[10] and does not decrease on irradiation at >320 nm.) The ir changes shown in Figure 2 indicate an approximately 50% drop in the photolysis rate of the ketones in the presence of Ni-3.

The product yields and ir data shown in Figures 1 and 2 indicate that the stabilizer Ni-3 can partially prevent the formation of photolysis products from ketones A and B. The cleavage of B to give acetone is a molecular process,[10] so that Ni-3 must be able to quench the excited macro ketone which is the precursor to cleavage. The cleavage of A to give carbon monoxide involves an initial scission to give free radicals[10] so that the drop in carbon monoxide production in the presence of Ni-3 might indicate quenching and/or free-radical scavenging. We have previously suggested that this stabilizer can scavenge some of the free radical products from polypropylene hydroperoxide photolysis.[2] However, the similarity in the effects of Ni-3 on the photolysis of PP-ketones A and B probably implies that quenching of the excited ketone is occurring in each case, regardless of whether Ni-3 can act as a radical scavenger. Ni-3 has previously been reported to quench the excited states of model ketones in the liquid phase by a somewhat inefficient collisional process.[8,9] It is not possible to deduce the nature of the solid-state quenching process from the above photolysis data due to the expected nonrandom distribution of the chelates and ketone groups within the film samples.[13]

Phosphorescence Quenching. Prior to irradiation, the PP-ketone films showed a broad phosphorescence at 77°K, centered at ~450 nm, with maxima at 420, 445, and 480 nm (excitation maximum at ~290 nm), similar to the published phosphorescence spectrum of poly(methylvinyl ketone).[14,15] This phosphorescence could not be detected at 25°, although a relatively strong fluorescence (at ~340 nm, excitation maximum ~290 nm) was observed at 77°K and persisted at 25°. This fluorescence has previously been attributed to traces of polynuclear aromatics,[16-18] which are probably absorbed from the urban atmosphere.[18] The long-wavelength tail of this fluorescence masked the weak PP-ketone fluorescence expected at ~400 nm.[14] Consequently only the phosphorescence emission can be used to monitor the concentration of excited carbonyl groups. In the presence of the stabilizers Ni-3 (0.18 wt %), Ni-4 (0.25 wt %), P-2 (0.40 wt %), and P-5 (0.5 wt %), the phosphorescence intensities of the PP-ketone films (~0.05 *M* in >C=O groups) at 77° were identical to that of a stabilizer-free film sample. [The fluorescence emission (from the polynuclear aromatics) was also unaffected by these stabilizers, except in the presence of P-5, when it was reduced to virtually zero.]

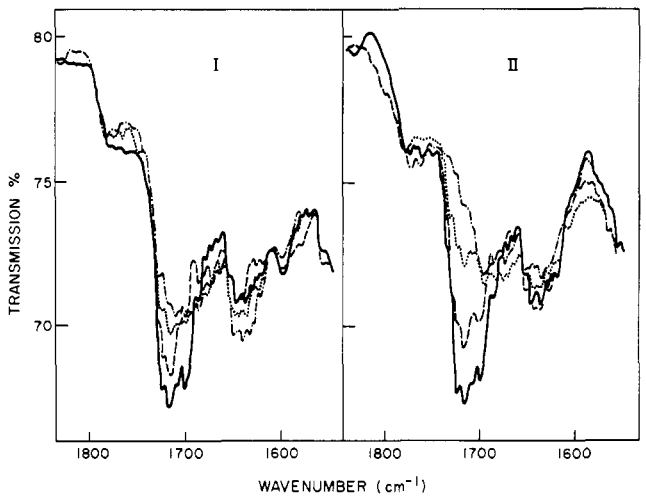


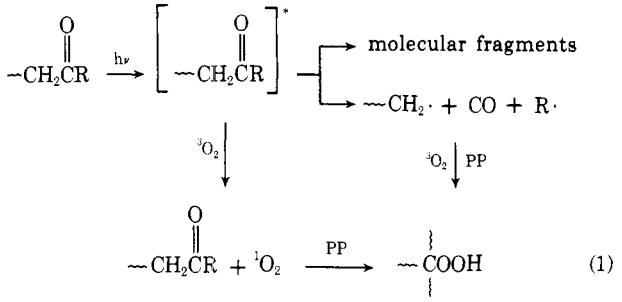
Figure 2. Vacuum photolysis of PP-ketone: ir changes. Film details and irradiation conditions as in Figure 1. Double thickness of film: (I) with Ni-3 (0.30 wt %); (II) stabilizer free. Irradiation periods were: (——) 0 hr, (----) 40 hr, (····) 66 hr, and (-·-·-) 119 hr.

The absence of phosphorescence quenching by these stabilizers indicates that the deactivation of ketone singlets or triplets suggested from the data in Figures 1 and 2 does not occur at 77°K in the rigid glassy PP, with the relatively low concentrations of stabilizers and >C=O groups employed here. Since the absorption spectrum of Ni-3[8] and the emission spectra of ketones[12] do have some overlap, Förster, long-range energy transfer may be theoretically possible between ketone excited states and Ni-3,[13] but is apparently unimportant in our polymer system at 77°K. The observed absence of PP-ketone phosphorescence quenching at 77°K, and the reduction in the ketone photolysis rate at 25° (above the glass transition of the polymer) is, however, consistent with a collisional deactivation of excited ketone states by the chelates since collisional quenching is dependent on the viscosity (rigidity) of the medium.[13] In addition any long-range energy transfer to the chelates would have been largely viscosity independent.[13]

Collisional quenching by 1-*cis*,3-*cis*-cyclooctadiene at 77°K in glasses has been reported for poly(methylvinyl ketones). Chien and Connor have previously reported the quenching of the phosphorescence of diethyl ketone in a frozen glass at 77°K by a Förster type of process.[6] However, the fluorescence which they detected at 340 nm was probably not from the ketone (fluorescence now accepted to be ~405 nm[14]), and their phosphorescence lifetime of ~2 × 10^{-2} sec is over an order of magnitude longer than the accepted ketone triplet lifetime.[19] Thus, although their phosphorescence wavelength (~447 nm) is consistent with a ketone, the lifetime is not and the reported chelate quenching of ketone triplets is probably incorrect.

PP-Ketone-Sensitized Photooxidations. The PP-ketone films were irradiated in air in the presence of various

stabilizers. The build-up of -OH (at ~3400 cm^{-1}) and >C=O (at ~1715 cm^{-1}) for each film are shown in Figure 3. In the abscence of stabilizers, the PP-ketone film photooxidized much more rapidly than films pressed from the same PP resin, but under nitrogen, *i.e.*, free of carbonyl substituents. In particular, although the N_2-pressed film gives an induction period for -OH build-up (mainly due to hydroperoxide[20]), an induction period is not observed with the PP-ketone film; in addition, the carbonyl content of this film probably actually decreases slightly in the first few hours of irradiation. This latter effect is consistent with the excitation of the PP-ketone groups to give some radical products *via* a Norrish type I process[10] and possibly singlet oxygen ($^1O_2$, $^1\Delta_g$),[21] both of which can then yield PP-hydroperoxide[18] (reaction scheme 1)



(1)

Thus a rapid hydroperoxide build-up is to be expected, at the expense of the initially high concentration of ketone groups. The hydroperoxide itself will also photolyze to generate some macrocarbonyl products,[20] but the generation of these carbonyl products will only become significant once an appreciable hydroperoxide concentration has accumulated.

Some caution must be exercised, however, in comparing the photooxidation rates of PP-ketone and the PP films shown in Figure 3 since appreciable chain scission occurs during the thermal oxidation required to produce the PP-ketone film. Thus the two samples will differ appreciably in molecular weight, as well as carbonyl content. Furthermore, previous attempts to demonstrate the effects of carbonyl substituents or impurities on polyolefin photooxidation are somewhat contradictory. Inclusion of long-chain aliphatic ketones with PP was found to have no effect on the photooxidation of PP,[22] whereas copolymerization of ethylene with carbon monoxide gave a more photosensitive polymer than low-density polyethylene.[23] Hutson and Scott have found that the photodegradation rate of high-density polyethylene is proportional to the carbonyl content introduced during processing[24] but this conclusion has not been supported for PP degraded during processing.[25]

The data shown in Figure 3 indicate that stabilizers P-5 and P-7 are extremely effective in preventing the photooxidation of PP-ketone, P-2 is moderately effective and Ni-3 and Ni-4 only weakly effective. These results are in marked contrast to the effects of these same stabilizers on the photooxidation of PP films containing PP-hydroperoxide (PPOOH), which we have described previously.[2] In the presence of PPOOH, Ni-3, Ni-4, P-2, and P-5 are all very effective inhibitors of the PP photooxidation, probably *via* radical scavenging processes since none of these is a thermal decomposer of PPOOH.[2]

The stabilization effects shown in Figure 3 cannot be explained by uv absorption alone. The relevant uv absorptions are Ni-3 (~17%), Ni-4 (~1.0%), P-2 (~5%), P-5 (~70%), and P-7 (~9%) as measured at 310 nm, the wavelength of maximum energy absorption from sunlight or the Xe arc (calculated from the PP-ketone uv absorption[10] and the spectrum of terrestrial sunlight[2]). The >C=O build-up in the presence and absence of the stabilizers (Figure 3) is particularly important in the interpretation of the stabilization effects. In the presence of Ni-3, >C=O build-up proceeds steadily from the onset of irradiation, whereas in the absence of stabilizers, the >C=O concentration probably falls slightly in the first 15 hr, and then increases rapidly. This difference supports the vacuum photolysis data which indicated that Ni-3 can reduce the rate of PP-ketone photolysis, although appreciable scission to radicals is still occurring as shown by the immediate increase in -OH build-up even in the presence of Ni-3. Ni-4 shows a very similar behavior to Ni-3. Stabilizers P-2 and especially P-5 and P-7 can prevent both the loss of >C=O and the formation of oxidation products for appreciable times. This seems to indicate that all of these last three can inhibit ketone photolysis, although in the case of P-5 its appreciable uv absorption effect (~70% of the incident light) will also contribute to a slower PP-ketone photolysis rate.

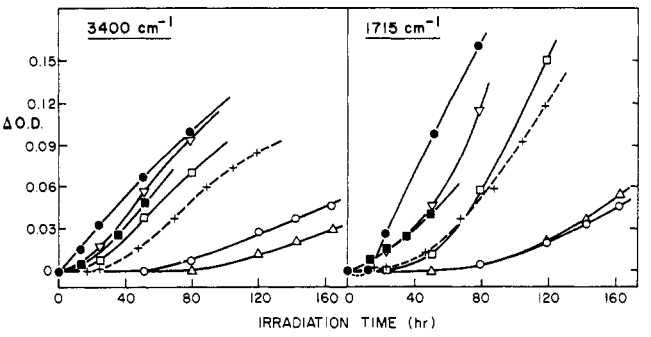


Figure 3. Photooxidation of PP-ketone films: ir changes. Xenon arc irradiation; PP-ketone film details as in Figure 1. ΔOD is the increase in optical density for each absorption. Stabilizers and concentrations: (●) none; (■) Ni-3, 0.18 wt %; (▽) Ni-4, 0.25 wt %; (□) P-2, 0.40 wt %; (○) P-5, 0.5 wt %; (△) P-7, 0.75 wt %; carbonyl-free PP film: (+).

We have previously shown that P-7 can quench the photolysis of model ketones in the liquid phase at a diffusion controlled rate ($k_q \sim 5 \times 10^9\ M^{-1}\ sec^{-1}$), yet P-2 and N-3 did not quench ($k_q < 5 \times 10^8\ M^{-1}\ sec^{-1}$) under the same irradiation conditions.[7] More recently P-5 has been reported to quench model ketones in the liquid phase at a diffusion-controlled rate,[7] whereas Ni-3 and Ni-4 are somewhat less efficient quenchers (~$3^{8,9}$ and ~5^8 times below the diffusion rate, respectively). Because of the problems involved in estimating quenching in the presence of such strong uv absorptions as some of these stabilizers possess, the agreement between the published values for liquid phase quenching is fairly satisfactory. From the liquid phase work and the data shown in Figure 3, there seems to be a fair correlation between liquid phase quenching rates and solid-state stabilization.

Association between the ketone substituents in the PP film and the stabilizers might also contribute to the greater effectiveness of the phenolic stabilizers (P-2, P-5, and P-7) as compared to Ni-3 and Ni-4, where the -OH groups of the phenolic ligands are involved, at least in part, in chelation.

In the liquid phase, oxygen quenching of excited ketones, probably to give $^1O_2$,[21] competes with quenching by stabilizers[7] so that $^1O_2$ production should be significant even in the uv stabilized polymer. However, nickel chelates are now well established as singlet oxygen quenchers (to give ground state oxygen), both in the liquid[18,26-28] and solid phase.[18,26] Ni-3 and Ni-4 can both quench $^1O_2$ to some extent, yet fail to appreciably retard the photooxidation of PP-ketone. This implies that radical generation, after

ketone photoexcitation, is a more important initiation process than is $^1O_2$ generation. In addition, P-2, P-5, and P-7 do not quench $^1O_2$[26] yet do retard the photooxidation of PP-ketone.

Conclusions

Some PP photostabilizers can prevent the photolysis of ketonic substituents in solid PP by quenching excited states, and so retard photooxidation of the polymer sensitized by these macro ketones. The scission of excited ketonic groups to give radical products is probably prevented by collisional processes, rather than by long-range energy transfer, and quenching may be enhanced by chromophore-stabilizer association. There seems to be a fair correlation between the stabilization of ketone-substituted PP and the available data on the quenching of ketone photolysis in the liquid phase by these same compounds.

References and Notes

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Polymerization and Dimerization of Vinylcarbazole. II.[1] Relation between Reactive Intermediates and Final Products in Irradiated Benzonitrile Solutions

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ABSTRACT: Reactive intermediates involved in the reactions of dimerization or polymerization were directly observed by use of a pulse radiolysis technique. The relation between reactive intermediates and final products was studied in irradiated benzonitrile solutions of vinylcarbazole. The cyclodimer and polymer were found to be produced in the aerated and deaerated solutions irradiated, respectively. The initiating species of both the radiation-induced dimerization and polymerization was confirmed to be the cation radical of vinylcarbazole. The polymerization proceeds *via* a cationic process. The reaction of the radiation-induced cyclodimerization is a chain reaction as well as the photochemically induced cyclodimerization. The kinetic chain length was estimated to be several hundreds. Oxygen was concluded to play an important role in the formation of the cyclodimer after the production of the cation radical of vinylcarbazole.

Few attempts[1,3-7] to study reactive intermediates involved in a radiation-induced polymerization have been done by means of direct observations. The information about the reactive intermediates related to polymerization or dimerization of vinylcarbazole initiated by charge-transfer or photo-chemical reactions has been usually obtained from indirect observations except for a few cases.[1,8,9] The identification and behavior of some reactive intermediates involved in the irradiated benzonitrile solutions were reported in our previous paper.[1] Both the direct observations of the reactive intermediates and the product analysis for the same solutions were found to be necessary to elucidate the detailed mechanism of complicated reactions such as the dimerization and polymerization. The present paper deals mainly with the relation between the reactive intermediates and the final products.

I. Experimental Section

Materials. Vinylcarbazole, benzonitrile, and biphenyl were purified in a manner identical with that recently described.[1] Naphthalene was Tokyo Kasei's zone-refined reagent. Triethylamine, aniline, and dimethylaniline were distilled and water was triply distilled.

Pulse Irradiation. The method of pulse radiolysis has been described.[10] Only an outline of the equipment relevant to this work is presented here. A 2.5–2.8-Mev electron beam from a van de Graaff accelerator was used throughout. The pulse duration ranged from 0.5 to 2.0 μsec and peak currents were usually used in the range 120–200 mA.

Dosimetry. The mean radiation dose delivered to the solutions was determined by use of the ferrocyanide chemical dosimetry.[11] The molar extinction coefficient, $\epsilon(Fe(CN)_6^{3-})$, at 420 nm was taken as 1000 M^{-1} cm^{-1} and $G(Fe(CN)_6^{3-})$ as 3.2 molecules/100 ev.

Irradiation Cells. Rectangular irradiation cells made of Su-