not occur because 65° is above the maximum polymerization temperature. The initiated mixture is promptly transferred to a warm mold having the shape of the object desired. Polymerization occurs immediately as soon as the temperature of the mixture in the filled mold falls below the maximum polymerization temperature. After 1 hr at 0° and overnight at room temperature, copolymer conversion is of the order of 80%. Homopolymer conversions are lower. Unreacted monomers are removed by extraction with acetone or methanol.

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O. Vogl, H. C. Miller, and W. H. Sharkey*

Contribution No. 1926
Central Research Department,
E. I. du Pont de Nemours and Co.
Wilmington, Delaware 19898

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Quenching of Ketone Photodecomposition Reactions and Polymer Stabilization

It has frequently been suggested that the deactivation of excited carbonyl impurities by certain effective commercial stabilizers is an important mechanism for the stabilization of polyolefins against actinic degradation.[1-3] In particular, long-range (Förster) energy-transfer processes have been invoked.[1,3] However, the reported experimental evidence for quenching relevant to polyolefin stabilization either has involved ill-characterized chromophores in the solid polymer[1] (chromophores which are probably aromatic impurities rather than carbonyl substituents[4]) or has involved evidence obtained indirectly from model compound experiments in the liquid phase, such as anthracene triplet quenching[2] and inhibition of ketone-sensitized photooxidations.[5]

We have studied the photochemistry of two ketones (2-methyl-4-pentanone and 2,6-dimethyl-4-heptanone) which are structurally related to the macro ketones (a terminal methyl ketone and a backbone ketone) which are reported to be the carbonyl species involved in the initiation of photooxidative degradation of polypropylene.[6] The effects of various reported quenchers and related compounds on the photolyses of these ketones were examined in spectroscopically pure hydrocarbon solutions at 30°. Dilute solutions of each ketone (~0.05 *M*) were irradiated with the filtered light from a mercury lamp (wavelengths >310 nm) and the degradation products analyzed by glc. Short-path-length cells (0.1 cm) and relatively low additive concentrations (0.04–0.6 wt %, comparable to the concentrations used in practice to stabilize polyolefins) were employed so that the quenching effects even of those additives which absorbed significantly in the near uv or which produced absorbing products could be followed.[7]

TABLE I
QUENCHING OF 2,6-DIMETHYL-4-HEPTANONE PHOTOLYSIS[a]

Quencher	Quencher concn range, $M \times 10^3$	Product τk_q M^{-1} [b]	
		i-C_4H_{10}	2-Methyl-4-pentanone
O_2	1.4–7.0		140 ± 20
cis-1,3-Pentadiene	13–43	>1000	70 ± 10
Diphenylamine	32–500	40 ± 4	110 ± 15
2,2′-Methylenebis(4-methyl-6-*tert*-butylphenol)	2.2–9.4	130 ± 13	130 ± 20
2,2′-Thiobis(4-*tert*-octylphenol)	0.9–14	450 ± 50	110 ± 10
Zinc dibutyldithiocarbamate	1.0–7.0	280 ± 30	90 ± 10
Zinc diisobutyl dithiophosphate	1.6–6.4	550 ± 50	~0

[a] Osram SP 500 mercury lamp, Corning C.S. 1-64 filter. Decahydronaphthalene solutions, oxygen free unless otherwise specified. Initial ketone concentration 0.050 *M*, 0.1-cm path cells. [b] Initial slope of the respective Stern–Volmer plots.

The quantum yields for isobutane (the only observed alkane) and 2-methyl-4-pentanone production during the irradiation of 2,6-dimethyl-4-heptanone were found to be 0.50 ± 0.005 and 0.20 ± 0.03, respectively, in degassed, additive-free decahydronaphthalene. Quantum yields for carbon monoxide and propylene production agreed with the values for isobutane and the pentanone respectively, but were of a lower experimental accuracy. At the conversions employed (<5%) over 85% of the consumed ketone was accounted for by the Norrish type I products (CO and isobutane) and II products (olefin and pentanone). Neither 2-methyl-4-butanal nor 2,6-dimethyl-4-heptanol was detected; alcohol formation *via* intermolecular hydrogen abstraction from the solvent can be expected to be slow in comparison with the rapid intramolecular abstraction (the type II process).[8]

Several commercial polyolefin uv-stabilizing compounds[9] were found to be ineffective in quenching the formation of types I and II products in decahydronaphthalene or *tert*-butylbenzene. These included 2,6-di-*tert*-butyl-4-methylphenol, octadecyl 3-(3′,5′-di-*tert*-butyl-4′-hydroxyphenol)-

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(7) The I_a' value at a given wavelength in the presence of an absorbing additive was estimated from the observed total absorbance of each cell, the incident light intensity and the extinction coefficient at that wavelength, and the ketone concentration. These I_a' values were then summed at 5-nm intervals across the effective ketone absorption spectrum (310 nm to 390 nm) to give the total absorbed intensity.

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propionate, [2,2′-thiobis(4-*tert*-octyl)phenolato](*n*-butylamine)nickel(II) and bis[2,2′-thiobis-(4-*tert*-octyl)phenolato]nickel(II) used in concentrations of up to 0.32 wt %. Only three of the additives examined, including those listed in Table I, caused the respective calculated ketone absorption values (I_a') to fall below 80% of the absorption (I_a^0) calculated for the additive-free ketone solutions (1.2×10^{-6} einstein l.$^{-1}$ sec^{-1}). For the more strongly absorbing additives, I_a' values ranged down to 5×10^{-6} einstein l.$^{-1}$ sec^{-1} (for diphenylamine, Table I) and 1.4×10^{-7} einstein l.$^{-1}$ sec^{-1} (for the two Ni(II) chelates) at the maximum concentrations employed. The correction for the significant absorption by the latter Ni(II) chelates could have obscured a small quenching effect by these compounds ($\tau k_q < 10\ M^{-1}$).

Compounds which were found to be effective in reducing the yields of photolysis products are listed in Table I. The observed quantum yield values in the presence of these additives gave Stern–Volmer plots which were initially linear; the initial slopes of these plots gave the τk_q values (lifetime of the excited state and quenching rate constant, respectively) shown in Table I. Experimental values for *cis*-1,3-pentadiene and dissolved oxygen quenching are included for comparison.

Irradiations of decahydronaphthalene solutions of 2-methyl-4-pentanone in the presence of the same additives as used with the heptanone gave very similar results with regard to additive quenching effectiveness. Quantum yields for isobutane and acetone (or propylene) production in the absence of quenching were found to be 0.010 ± 0.001 and 0.10 ± 0.01, respectively; the carbon monoxide quantum yield was always <0.0008.

The 1,3-pentadiene quenching data in Table I lead to a lifetime of $\sim 1 \times 10^{-8}$ sec for the excited state (probably the triplet) of 2,6-dimethyl-4-heptanone, if diffusion control is assumed.[10] This lifetime is in good agreement with the value ($\sim 1.5 \times 10^{-8}$ sec) calculated from the data of Bibart, *et al.*,[11] for the intramolecular abstraction of primary hydrogens from 2-pentanone, at low degrees of photolysis. The τk_q values (Table I) for the quenching of 2-methyl-4-pentanone formation by other additives are all quite similar, and quenching probably occurs at or close to the theoretical rate for diffusion-controlled processes in all cases. Hydrogen bonding between some additives and the ketone might allow collisional quenching at rates slightly greater than those anticipated from the bulk viscosity. Turro and Engel[12] have proposed that biacetyl quenching proceeds *via* a reversible hydrogen abstraction from phenols and by an electron or charge-transfer mechanism for aromatic amines. These mechanisms might also influence the collisional quenching of some of the compounds listed in Table I. The apparent τk_q values for isobutane production will, of course, reflect both the quenching effectiveness and the radical-scavenging efficiency of the additives. For example, the zinc diisobutyl dithiophosphate data indicate that the additive is not a quencher of the excited ketone states, but functions solely as an efficient $i\text{-C}_4\text{H}_9\cdot$ trap.[13]

The nickel(II) chelates studied do not appear to quench the Norrish type I process (to give mainly $i\text{-C}_4\text{H}_9\cdot$) or type II process (to give mainly 2-methyl-4-pentanone). This result is in disagreement with the conclusions of Chien and Conner[5] who showed that the photooxidations of isopropylbenzene solutions sensitized by 3-pentanone are retarded by a [2,2′-thiobis(4-*tert*-octyl)phenolato]nickel(II) complex. This retardation was attributed to a Förster type of long-range energy-transfer process. We have confirmed that certain nickel thiophenolate complexes do inhibit the initiation of ketone-sensitized photooxidations.[14] However, we conclude that this inhibition is probably attributable to the nickel chelates efficiently quenching singlet oxygen[15] which is involved in some ketone-sensitized photooxidations,[16] rather than attributable to the quenching of the excited ketone.

Collisional quenching in a solid polymer may be possible to some extent, since Heskins and Guillet[17] have shown that a 1,3-diene can quench the photodecomposition of ethylene–carbon monoxide copolymers, both in the liquid and solid phases. However, quenching was relatively inefficient in the latter case. The possibility of long-range energy transfer between ketonic impurities and uv stabilizers in solid polyolefins is not precluded by our data, but obviously requires further investigation.

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(10) Solution viscosity in decahydronaphthalene at 30° was 1.9 cP. Then $k_q = 4 \times 10^9\ M^{-1}$ sec^{-1}, calculated from the modified Debye equation.

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D. J. Carlsson,* D. E. Sproule,[18] D. M. Wiles

Division of Chemistry
National Research Council of Canada[19]
Ottawa K1A OR9, Canada

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Crystalline Poly(DL-β-isopropyl-β-propiolactone)

The crystalline structure of the naturally occuring polyester, poly(D-β-hydroxy butyrate) (PHB) has been reported to be a compact right-handed helix with a twofold screw axis along the chain.[1] The same optically active polymer[2] and its

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