Photochemistry of Ketone Polymers. IX. Triplet Energy Transfer in Poly(vinyl ketones)

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ABSTRACT: Studies have been made of electronic energy transfer from the triplet state of carbonyl groups in poly(methyl vinyl ketone) (PMVK), using 1-*cis*,3-*cis*-cyclooctadiene (COD) as a triplet quencher. About 70-75% of the photochemical reaction leading to scissioning of the polymer originates from the triplet state. The lifetime of this state is estimated as 6 nsec. Phosphorescence quenching results show that in solid solution at 77°K, triplet migration takes place in poly(phenyl vinyl ketone) (PPVK), but not in PMVK or poly(methyl isopropenyl ketone) under these conditions.

The importance of ketone groups in the photodegradation of many polymeric materials is now well established. Guillet and Norrish[1] first showed that the photolysis products of PMVK in solution could be explained on the basis of the Norrish type I and type II reactions of low molecular weight ketones. Wissbrun[2] later demonstrated that similar reactions occurred in the photolysis of solid films of PMVK, whereas poly(methyl isopropenyl ketone) (PMIPK) degraded quantitatively to monomer. The photochemistry of poly(phenyl vinyl ketone) (PPVK), ethylene-carbon monoxide polymers, and copolymers of MVK and PVK have since been studied in this laboratory.[3-6]

Energy transfer studies have proved to be very useful in the investigation of many photochemical systems. The changes in the yields of both chemical products and emitted light have been monitored to obtain information about the properties of excited states. The cyclic diolefin, 1-*cis*,3-*cis*-cyclooctadiene (COD) has been shown to be an effective triplet quencher in the type II photolysis reactions of Et-CO and PVK polymers in fluid solution.[4,6] On the other hand, David *et al.*[7-9] have studied the sensitization of naphthalene phosphorescence in PMVK, PPVK, and poly(vinyl benzophenone) (PVB) films at 77°K. In this study we have used COD as a triplet quencher in the photolysis of PMVK to estimate the triplet lifetime of this polymer in ethyl acetate solution using 313-nm radiation. The quenching of the phosphorescence of PMVK, PMIPK, and PPVK in solid solutions of H_4furan-ether at 77°K has also been used to investigate intramolecular triplet energy migration. Hunter *et al.*[10] have demonstrated previously that the efficiency of transfer of benzophenone triplet energy to a naphthalene guest is a factor of ~10^3 greater in a benzophenone crystal than in a benzophenone glass, showing that molecular order contributes significantly to the efficiency of triplet excitation migration.

Experimental Section

Materials. PMVK and PMIPK were prepared from freshly dried and distilled monomer. A 30% solution in ethyl acetate was degassed and kept at 60° overnight with benzoyl peroxide added. The polymer was reprecipitated three times into cooled methanol and then freeze-dried. PPVK was the bulk polymerized sample B37 described in a previous publication.[6]

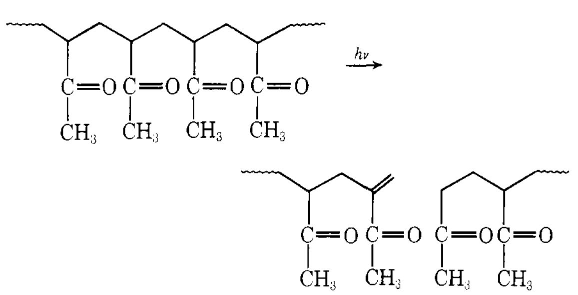
Ethyl acetate from Fisher was dried over K_2CO_3 for 1 week, filtered, and distilled. The distillate was refluxed over P_2O_5 until no absorption above 280 nm was observed, and then it was redistilled. COD from Fisher was purified on an Aerograph Autoprep gas chromatograph (purity >99.8%, ϵ ~0.05 at 313 nm). H_4furan and ether were freshly distilled from $LiAlH_4$ and sodium, respectively.

Photolysis of PMVK. Solutions of PMVK in ethyl acetate were irradiated at 313 nm with the apparatus previously described.[3] The solutions were degassed by freeze-thaw cycles and sealed under vacuum. The molecular weight changes were followed on a Waters Ana-Prep gel permeation chromatograph. The GPC calibration curve for PMVK was determined by the use of a search program similar to that of Balke and Hamielec[11] using the number-average molecular weights of two different samples of the polymer determined by osmometry.

Phosphorescence Measurements. Spectra were recorded on a Hitachi Perkin-Elmer MPF-2A spectrophotometer fitted with a phosphorescence accessory including a chopper to eliminate prompt signals to the photomultiplier. Cells were 2-mm quartz tubes which fitted into a liquid nitrogen dewar. Relative emission intensities were obtained from areas of right-angle, ratio-recorded band spectra.

Results and Discussion

PMVK Photolysis. After the absorption of uv light by carbonyl groups the Norrish type II reaction causes a split in the C-C backbone of the PMVK polymer and results in a decrease in the average molecular weight.



(1)

The number of chain breaks per molecule is given by

$$\left[\frac{(\bar{M}_n)_0}{(\bar{M}_n)} - 1\right]$$

where $(\bar{M}_n)_0$ and $(\bar{M}_n)$ are the number-average molecular weights before and after irradiation, respectively. Thus the quantum yield (ϕ_{cs}) of chain breaks is given by

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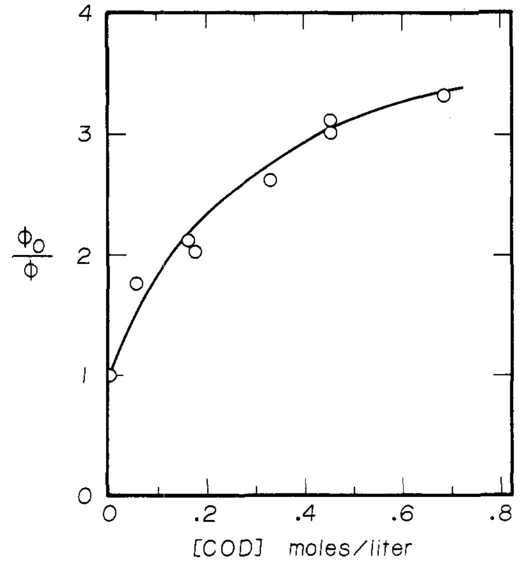

Figure 1. Stern-Volmer plot of quenching of chain scissioning reaction of PMVK by COD in ethyl acetate (25°).

$$\phi_{cs} = \left(\frac{(\overline{M}_n)_0}{(\overline{M}_n)} - 1\right)\frac{1}{I_a(\overline{M}_n)_0} \tag{2}$$

where I_a is the number of einsteins absorbed per gram of polymer. The value of ϕ_{cs} for PMVK has been reported recently from this laboratory[5] ($\phi_{cs} = 0.04 \pm 0.02$) and by Guillet and Norrish[1] ($\phi_{cs} = 0.034$). Quantum yield measurements in the absence and presence of a quencher are generally expressed in the form of the Stern-Volmer relationship

$$\frac{\phi_0}{\phi} = 1 + k_q\tau[\mathrm{Q}] \tag{3}$$

where ϕ_0 is the quantum yield in the absence of quencher and ϕ is the quantum yield at quencher concentration [Q], τ is the lifetime of the excited state in the absence of quencher, and k_q is the rate constant for energy transfer. In the simple case ϕ_0/ϕ *vs.* [Q] is a linear plot of slope $k_q\tau$ from which τ may be derived by assuming $k_q \sim k_{\mathrm{diff}}$, the rate constant for diffusion.

The results for the quenching of PMVK chain scission with COD are shown in Figure 1. The curvature is similar to that observed for COD quenching of Et-CO polymers[4] and may be interpreted in the same way. At the low concentrations used, COD quenches the triplet state and the cleavage from the excited singlet state remains practically unchanged. Dienes have been shown to quench ketone singlet states only at much higher concentrations.[12] However, when the COD quenches all the triplet state molecules, the curve tends to level out to provide a relative estimate of the singlet contribution. It is observed that the singlet contribution to PMVK chain scissioning is about 25-30%. Lukac *et al.*[13] reported an estimated of 35-50% for this value from quenching studies with 2,5-dimethyl-2,5-hexadiene. In any case, the estimated value is low compared to Et-CO polymers where the type II is approximately equally divided between singlet and triplet states.[4]

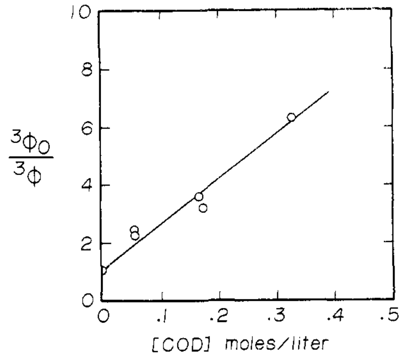

Figure 2. Stern-Volmer plot of triplet quenching of PMVK by COD in solution.

When the singlet contribution to ϕ_{cs} is subtracted, the Stern-Volmer plot for cleavage from the triplet state shows the normal characteristics. The $^3\phi^0/^3\phi$ *vs.* [COD] plot shown in Figure 2 is linear and the slope gives a value for $k_q{}^3\tau$ (16 l. mol^{-1}).

The choice of a value for k_q in order to estimate τ has become a question of some uncertainty.[14] It has been reasonably assumed that k_q is directly related to the diffusion coefficients of the reacting species. The probability, *p*, of energy transfer during an encounter may be less than unity and a correction for this must be made from an independent energy transfer system for which the donor lifetime is known. It is assumed that the efficiency of both processes compared are similar. We have chosen to use the value of *p* determined from the quenching of the fluorescence of small ketones with biacetyl in ethyl acetate[14] ($p \sim 0.23$) and further assumed that polymer diffusion may be neglected as being small compared with that of the quenching molecule. This affords an estimate of $^3\tau$ equal to 6 nsec. This compares with $\tau = 14$ nsec for ethylene-CO polymers[4] in which a value $p = 0.34$ was used. The smaller value of the Stern-Volmer slope, and presumably the shorter triplet lifetime, is consistent with the increased radiationless decay involving the primary C-H bonds of the α-methyl group in PMVK.[14,15] Ethylene-CO has only secondary α-carbon atoms adjacent to the excited ketone.

Phosphorescence Quenching. David *et al.*[7-9] have used measurement of the phosphorescence quenching of PVB and PPVK films containing naphthalene to show that the energy exchange distances were larger than the usual molecular collision diameters. However in PMVK films the usual value for exchange interaction ($R_0 \sim 11$ Å) was obtained.[8] Intramolecular triplet energy migration was invoked to explain the high R_0 values for the aromatic ketone polymers.

Analogous quenching experiments have been carried out in our laboratory but using COD as a triplet quencher, and in solid solutions of H$_4$furan-ether rather than films. The results are entirely consistent with the sensitization data of David *et al.* The quenching of phosphorescence of the carbonyl groups as a function of the COD concentration is well described by the Perrin relationship

$$\frac{I_p{}^0}{I_p} = \frac{\phi_0}{\phi} = e^{vN'C} \tag{4}$$

where v is the volume of a quenching sphere (cm^3), N' is 6.02×10^{20}, and $I_p{}^0$ and I_p are the phosphorescence intensities in the absence and presence of COD at concentration [C], respectively. The model assumes that any excited chromophore having a quencher molecule within a critical sphere of volume v, will inevitably be deactivated by

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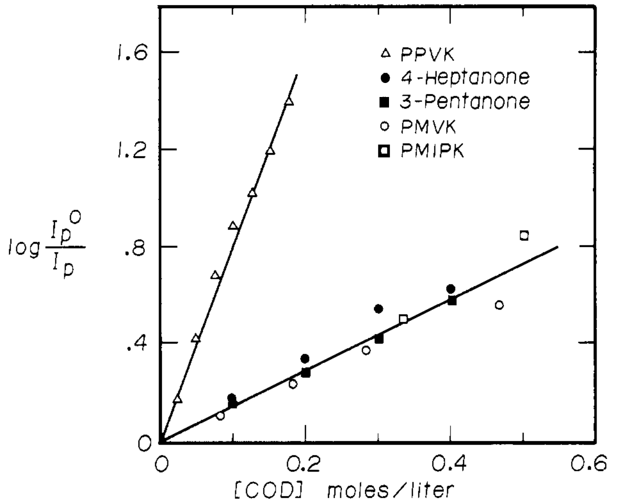

Figure 3. Phosphorescence quenching with COD in H_4furan–ether at 77°K.

energy transfer. Plots of log I_p^0/I_p *vs.* [COD] for the polyketones and for small ketones are shown in Figure 3. The size of the quenching spheres are similar for PMVK, PMIPK, and for the small ketones, whereas for PPVK the critical sphere has a radius R_0 = 19 Å. If the energy transfer in the polymer is random,[16] some intermolecular migration may take place where the local chromophore concentration is high, as in the films. The smaller value of R_0 in solid solution could imply that this intermolecular contribution is not shown in solid solution at low chromophore concentrations. Alternatively, migration of the triplet excitons may be dependent on the nature of the frozen matrix. In any case, energy migration does take place in the aromatic ketone polymers where it does not in the aliphatic polymers.

George[17] has recently considered models for triplet quenching when exciton diffusion takes place and has outlined two extreme cases in polymers. Energy trapping may be limited either by the final $M \rightarrow Q$ transfer step (M is the unit chromophore), or on the other extreme, by the rate of migration $M \rightarrow M$. We have observed that in the case of phosphorescence quenching of naphthalene polymers[16,18,19] the Stern–Volmer diffusion model describes the results, whereas in the case of the ketone polymers, the static Perrin model is more appropriate. In both cases the results demonstrate that intramolecular triplet migration takes place. However, it would seem that in the case of the aromatic π,π^* triplet states, the trapping is tending to the limit controlled by M–M migration, whereas in the case of the n,π^* ketone triplet states, the migration is faster than the final transfer step. A theoretical approach to this question seems justified.

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Photochemistry of Ketone Polymers. X. Chain Scission Reactions in the Solid State

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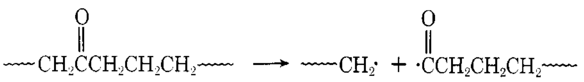
ABSTRACT: The quantum yield of chain scission was determined in the solid state for a number of polymers containing pendant ketone groups. Copolymers of methyl methacrylate with methyl vinyl ketone (PMMA-MVK) and styrene with phenyl vinyl ketone (PS-PVK) showed higher quantum yields with increasing temperature in the glassy state. Above the glass transition temperature (T_g) the quantum yield for chain scission increased rapidly to the same value as that obtained for the same polymer in solution. A homopolymer of phenyl vinyl ketone (PPVK) showed the opposite effect below T_g, but above T_g a constant quantum yield equal to the solution value was obtained. The variation in quantum yields is interpreted in terms of polymer chain mobility.

The degradation of polymeric materials on outdoor exposure can often be attributed to photochemical reactions arising from absorption of ultraviolet radiation by ketone groups present on the polymeric backbone. In polyethylene, for example, the ketone groups are known to be formed by air oxidation on extrusion and moulding.

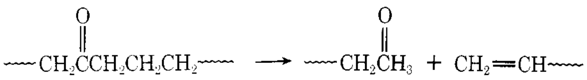
It has been shown[1-4] that ketones in polymeric material undergo some of the same photochemical reactions as their low molecular weight analogs. The most important of these are the Norrish type I and type II reactions. In polymers where the carbonyl carbon is on the backbone, both of these reactions will lead to lowering of the molecular weight.

Type I



$$\text{—CH}_2\overset{\text{O}}{\overset{\|}{\text{C}}}\text{CH}_2\text{CH}_2\text{CH}_2\text{—} \longrightarrow \text{—CH}_2\cdot + \cdot\overset{\text{O}}{\overset{\|}{\text{C}}}\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$$

Type II



$$\text{—CH}_2\overset{\text{O}}{\overset{\|}{\text{C}}}\text{CH}_2\text{CH}_2\text{CH}_2\text{—} \longrightarrow \text{—CH}_2\overset{\text{O}}{\overset{\|}{\text{C}}}\text{CH}_3 + \text{CH}_2\text{=CH—}$$

When the ketone group is on a side chain, the type I reaction will not cause scissioning of the main chain and only

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