Photochemistry of Ketone Polymers. VII. Polymers and Copolymers of Phenyl Vinyl Ketone

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ABSTRACT: Studies have been made of the quantum yield of chain scissioning of poly(phenyl vinyl ketone) and a PVK–styrene copolymer in benzene solution at 313 nm. The quantum yields were 0.25 and 0.18, respectively. Studies were also made of electronic energy transfer from the triplet excited states of carbonyl groups in these polymers, using 1-*cis*,3-*cis*-cyclooctadiene as a triplet quencher. Energy transfer from the homopolymer was shown to follow the normal Stern–Volmer relationship. A curved Stern–Volmer plot was obtained for PVK–styrene copolymers believed to be due to differences in the triplet lifetimes of isolated and sequential carbonyl groups. The excited-state lifetimes of the carbonyl groups in polymer molecules were estimated and found to be of the same order of magnitude as those in analogous model compounds.

Most polymeric materials undergo severe degradation when exposed to ultraviolet light, and one of the more important factors in "weathering" is the absorption of sunlight by the polymer. However, many pure synthetic materials such as polyethylene and polystyrene do not absorb in the range of wavelengths of solar radiation incident at the earth's surface (*i.e.*, $\lambda > 300$ nm). Their photodegradation is attributed to the incorporation of absorbing groups during manufacture or processing and one of the more common of these is the ketone carbonyl group.[1–5]

The photochemical reactions of low molecular weight ketones were first shown to occur in polymeric systems by Guillet and Norrish.[6] They showed that the photolysis of poly(methyl vinyl ketone) in solution could be explained on the basis of the Norrish type I and type II reactions. The same reactions were later shown by Wissbrun to apply when the polymer was photolyzed as a solid film.[7] Similar reactions were shown to be responsible for the chain scissioning of poly(ethylene-*co*-carbon monoxide).[8] Such copolymers may be considered to be polyethylene chains with carbonyl groups situated randomly in the chain backbone. By determining the quantum yields of the Norrish types I and II reactions for symmetrical dialkyl ketones, Hartley and Guillet[8,9] observed that these yields decreased and approached the relatively low yields measured for the copolymer. Thus in this case the polymeric environment leads to a considerable decrease in the amount of photochemical reaction. However, in the case of the methyl *n*-alkyl ketones, the type II quantum yield decreases very little with increasing chain length,[10] and the type II yield for aryl alkyl ketones remains substantially constant with increasing chain length.[11] Thus it is reasonable to suspect that polymers containing pendant chromophoric groups of the $C_6H_5C(=O)$– would behave differently than those containing aliphatic carbonyl groups in the polymer backbone.

David, Demarteau, and Geuskins[12] have reported that the quantum yield of chain scissioning of poly(phenyl vinyl ketone) (PPVK) was of the same order as the type II quantum yield of a "model compound" butyrophenone, and Golemba and Guillet[13] confirmed that the quantum yields of chain scissioning of PPVK and a copolymer of styrene and phenyl vinyl ketone were 0.25 and 0.18, respectively, approximately an order of magnitude higher than the yield determined for poly(ethylene-*co*-carbon monoxide). It therefore appeared to be of interest to study this system further, since it represents a highly efficient photochemical reaction in a polymer system.

Experimental Section

Apparatus. The source of light, filters, power supply, temperature controller, and photomultiplier have been previously described.[10] Two different types of cells were used with path lengths of 0.1 and 2.0 cm. The former was used when the decrease in molecular weight of a polymer was followed by gel permeation chromatography and the latter when this decrease was followed by viscosity measurements. These cells are schematically represented in Figure 1. Viscosities were measured in a water bath, the temperature of which was controlled to 25 ± 0.05°.

Materials. The polymers used in this study were copolymers of phenyl vinyl ketone and styrene and a homopolymer of phenyl vinyl ketone.

Phenyl vinyl ketone was prepared from 3-chloropropiophenone by dehydrochlorination using potassium acetate. The crude monomer was distilled under vacuum and the pale yellow liquid stored at −5° in the dark.

Phenyl vinyl ketone was polymerized in bulk under vacuum at 60° using lauroyl peroxide as initiator. The ultraviolet spectrum of this polymer (B37) is shown in Figure 2.

A polymer of styrene(s) and phenyl vinyl ketone (PVK) was prepared using lauroyl peroxide as initiator. Light was excluded during all stages of synthesis and recovery. The monomers were polymerized in bulk to approximately 50% conversion, the initial ratio being 19:1 (v/v) styrene to PVK. This polymer was designated B43. A second copolymer B43f was prepared by fractionating B43 using benzene as solvent and ethanol as precipitant. The fractionation was carried out in a photographic dark room with filtered lighting. Ethanol was added to the polymer solution until approximately two-thirds of the polymer had precipitated. The supernatant solution was decanted and the precipitated polymer recovered. The polymer was then dissolved in benzene and freeze-dried.

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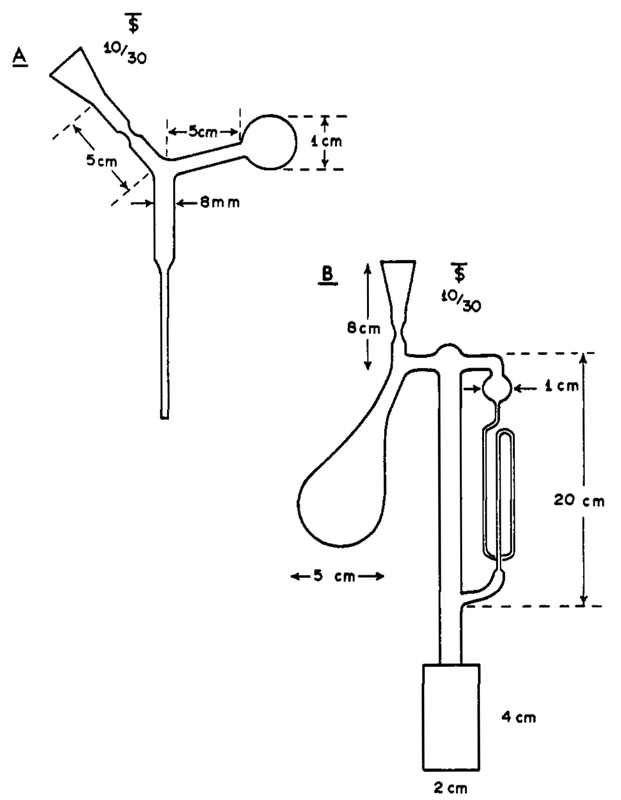

Figure 1. Photolysis cells: (A) 1-mm path length (0.3 ml), (B) 2-cm path length.

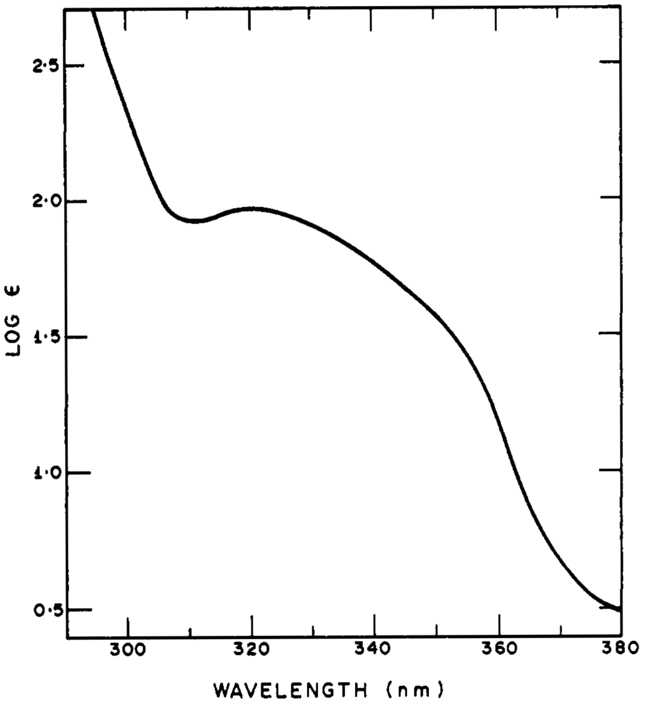

Figure 2. Uv absorption spectrum of poly(PVK) in benzene.

The mole per cent of phenyl vinyl ketone units in the copolymers was calculated from the measured extinction coefficient of the polymer and the absorbances of the copolymers at 323 nm. The copolymers B43 and B43f contained 9 and 14 mol % phenyl vinyl ketone units, respectively.

Benzene was used as the solvent in these photolyses and was purified in the following manner. Fisher "spectranalyzed" benzene was shaken with one-tenth its volume of concentrated sulfuric acid for 4 hr. The benzene was then washed with distilled water and dried with calcium chloride. It was then filtered, was dried over sodium, and then was distilled from sodium. The benzene was stored in a brown bottle and was transparent at 313 nm.

cis-1,3-Cyclooctadiene (COD) was purchased from Aldrich and purified either by distillation on a spinning band column or by preparative gas chromatography. Both methods gave samples better than 99.9% pure as judged by gas chromatography.

Photolysis of the Copolymer B43. To the dry cell (Figure 1B) was added, volumetrically, a previously prepared polymer solution, which nominally contained 0.4 g of polymer per decaliter. This concentration of the polymer absorbed 50% of the incident light. Any additive such as COD was also combined in this solution. The total volume was usually 22 ml. When the solution was degassed under vacuum, the procedure was as follows: the solution was transferred to the bulb and frozen by lowering the temperature to −180°, evacuated to less than 10^{-4} Torr, and then isolated as the contents were allowed to melt. This procedure was repeated four to five times, and then the cell was sealed under vacuum during the final freeze–pump step. When the solution was irradiated in the presence of air the cell was stoppered.

The cell was transferred to a water bath thermostated at 25°. The viscometer area of the cell was filled and the flow time to pass two reference marks was measured. This was repeated until 0.5% reproducibility was obtained. The flow time of the solvent was measured in a similar manner previous to the experiment.

As the polymer solutions were sensitive to the laboratory lighting, care was taken to exclude light during their preparation. Polymer solutions were stored in brown bottles, if storage was necessary. The Pyrex section of the irradiation cell, including the capillary and degassing bulb, was coated with amber paint and annealed. The color of the stain filtered out light capable of degrading the polymer while flow times were being measured. During this period the quartz section of the cell was covered with black cloth.

The polymer solutions were irradiated and the light absorbed determined by monitoring the incident and emergent intensities before, during, and after photolyses with a calibrated photomultiplier. The photolyses were interrupted periodically to measure flow times. The alternation of photolysis and viscometry measurements was repeated up to a point corresponding to 0.5 to 1.0 break per polymer chain.

The viscosity relationship used was

$$[\eta] = (1.13 \times 10^{-4})M^{0.73}$$

This equation[14] was derived for viscosities of narrow distribution polystyrenes measured in benzene at 25°, and K and α were constant over a broad range of molecular weight.

Photolyses of the Copolymer (B43f) and the Homopolymer (B37). The change in the molecular weight of these polymers was measured by gel permeation chromatography. Approximately 0.5 ml of solution containing the amount of polymer required to absorb about 50% of the incident light (10 or 25 mg of the copolymer or homopolymer (respectively) was irradiated in a 0.1-cm quartz cell (Figure 1) and stored in the dark until injected onto the column.

Determination of Limiting Viscosity Number. The limiting viscosity number $[\eta]$ was found by plotting η_{sp}/c and ln η_{rel}/c against concentration and extrapolating to zero concentration. The Huggins equation $\eta_{sp}/c = [\eta] + [\eta]^2kc$ describes the shape of η_{sp}/c *vs. c* plot. For both the Desreux and irradiation viscometers the flow times were sufficiently long so that no kinetic corrections were necessary and the value of the Huggins constant k was determined to be 0.162 for benzene, which was used to evaluate $[\eta]$ when viscosities were measured at only a single concentration in the irradiation cell.

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[14] M. Kurata, M. Iwama, and K. Hamada in "Polymer Handbook," J. Bandrup and E. H. Immergut, Ed., Interscience, New York, N. Y., 1966.

Determination of Quantum Yield. The quantum yield of chain scission ϕ_{cs} is equal to

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

where $(\bar{M}_n)_0$ and $\bar{M}_n$ are the number-average molecular weights of the polymer before and after degradation, respectively. I_A is the number of einsteins absorbed per gram of polymer.

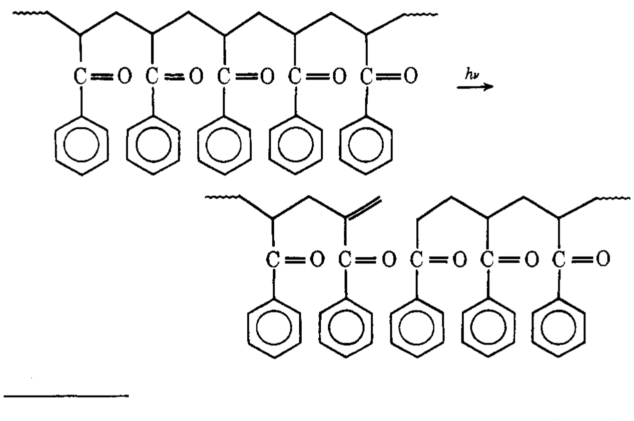
Determination of Number-Average Molecular Weights. Changes in the molecular weight of the homopolymer B37 and the copolymer B34f were measured using a Waters Associates Ana-Prep chromatograph with tetrahydrofuran solvent and columns packed with Styragel, calibrated with narrow-distribution polystyrene standards obtained from Waters Associates and Pressure Chemical Corp. Calibration curves were checked regularly by injection of 0.1 w/v solutions of standard samples. Duplicate injections were made for photolyzed samples of B43f. The number-average molecular weight of each sample was computed from the moments of the chromatograms calculated by Gaussian quadrature.

It was assumed in calculating the number-average molecular weight of the phenyl vinyl ketone polymers that the volume of solution of a poly(phenyl vinyl ketone) molecule was the same as that of a polystyrene molecule of the same degree of polymerization. After correction for the difference in weight between styrene and phenyl vinyl ketone units, the reasonably close agreement between molecular weights determined by osmometry and gel permeation chromatography suggested that this assumption is approximately valid, although the GPC results are consistently about 10% lower (Table I). Since this is a consistent error, it will have only a minor effect on quantum yield determination.

The precision of measurements using GPC was about 5%, but the starting number-average molecular weights varied over a larger range than this, probably because of the degradation of the polymers by laboratory lighting. To compensate for this, the molecular weights of the starting and irradiated material were measured for each experiment.

Results and Discussion

Poly(phenyl vinyl ketone) and copolymers of phenyl vinyl ketone and styrene were irradiated in benzene solution with light of wavelength 313 nm. The homopolymer displays a low-intensity absorption band ($\epsilon_{max}{}^{323}$ 100) in the 300–350-nm region. This is similar to the absorption band for butyrophenone which has been assigned to an n-π^* transition.[15] At the wavelength of irradiation only the carbonyl chromophores in the side chain of these polymers absorb energy. The major photochemical reaction is the Norrish type II split which causes a rupture of the C–C backbone resulting in a decrease in the average molecular weight of the polymer.



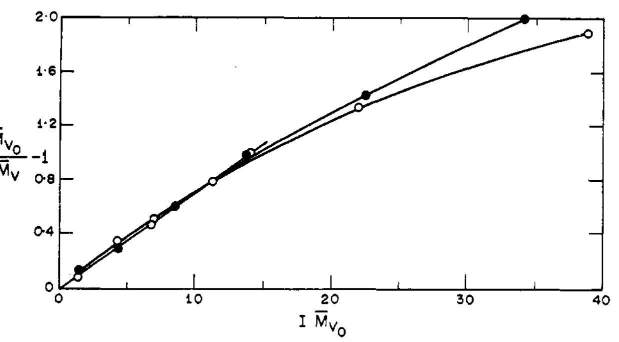


Figure 3. Photolysis of S–PVK copolymer B43 in benzene solution: (○) *in vacuo*, (●) in air.

Table I
Number-Average Molecular Weights, $\bar{M}_n$

Polymer	GPC	Osmometry
B43	160,000	171,000
B43f	75,000	85,000
B37	65,000	75,000

Photolysis of the Copolymer B43. Figure 3 shows a plot of $[(\bar{M}_v)_0/\bar{M}_v] - 1$ *vs.* $I(\bar{M}_v)_0$ for the irradiation of 0.4 w/v solutions of B43 in benzene at 25°, a degassed solution under vacuum, and a solution photolyzed in the presence of air.

In both cases the slopes are initially constant but decrease as the amount of degradation increases. The breadth of the distribution ($\bar{M}_w/\bar{M}_n$) of polymers prepared by free-radical polymerization is usually greater than 2. Thus, as degradation proceeds the distribution will also change and the slope will deviate from linearity. For this reason the initial slope was calculated and values of 0.072 and 0.070 were obtained *in vacuo* and in air, indicating that the quantum yield of chain scissioning (ϕ_{cs}) was not affected by the oxygen present in solution.

For sample B43, the ratio $\bar{M}_w/\bar{M}_n$ was found to be 2.6 by GPC measurements. $\bar{M}_v$ was determined from the GPC trace by the equation

$$M_v = \left(\frac{\sum n_i M_i^{1.73}}{\sum n_i M_i}\right)^{1/0.73}$$

and $\bar{M}_v/\bar{M}_n$ was calculated to be 2.4. The quantum yield of chain scissioning of this polymer was thus estimated to be 0.070 × 2.4 = 0.17.

Since $\bar{M}_w/\bar{M}_n$ is greater than 2 an error is introduced by assuming the identity of $(\bar{M}_v)_0/\bar{M}_v$ with $(\bar{M}_n)_0/\bar{M}_n$, but it can be shown that the error is not large ($\sim$10%). In spite of these approximations, the viscosity technique led to two important observations: (1) dissolved air did not affect the quantum yield of chain scissioning and (2) ϕ_{cs} for the copolymer is relatively high and of the order of 0.2.

If the types I and II photochemical reactions are solely responsible for side and main chain cleavages, respectively, ϕ_{cs} is a measure of the type II reaction. Although type I cleavage would result in a slight decrease in the number-average molecular weight of the polymer due to loss of benzoyl groups the viscosity of the solution would not be affected since the decrease in polymer size is negligible.

Photolysis of the Copolymer B43f and the Homopolymer B37. Table II shows the data obtained for the photolysis of

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[15] J. N. Pitts, Jr., L. D. Hess, E. J. Bau, E. A. Schuck, J. K. S. Wan, P. A. Leermakers, and G. Vesley, *Photochem. Photobiol.*, 4, 305 (1965) (see p 314).

TABLE II
PHOTOLYSIS OF COPOLYMER B43f IN BENZENE AT 25°. DETERMINATION OF ϕ_{cs}

$(\overline{M}_n)_0$	$[(\overline{M}_n)_0/\overline{M}_n] - 1$	ϕ_{cs}
71,500	0.08	0.17
71,500	0.17	0.13
71,500	0.18	0.20
78,400	0.38	0.22
74,500	0.48	0.19
74,500	0.49	0.18
74,500	0.54	0.17
74,500	0.64	0.21
78,400	0.68	0.20
78,400	0.71	0.15
78,400	0.87	0.13
78,400	1.54	0.16
		Mean 0.176 ± 0.02

B43f. The value of ϕ_{cs} was found to be 0.176 with a standard deviation of ±0.02, which is in good agreement with that estimated for copolymer B43 by viscometry. From the data shown in Table III, a value of ϕ_{cs} of 0.245 ± 0.015 was measured for the homopolymer at 313 nm in benzene solution at 25°, which is very close to the value of 0.22 obtained by Lukac, *et al.*,[16] for photolysis in benzene at 366 nm. Thus both the homopolymer and copolymer have a relatively high quantum yield of chain scissioning as compared to other carbonyl-containing polymers such as poly(ethylene-*co*-carbon monoxide)[8] and poly(methyl vinyl ketone).[6,7]

Evidence for the Type II Reaction. In another experiment, both the copolymer (B43f) and the homopolymer were irradiated in deaerated benzene solution at 25° to high doses (approximately 10^{-2} einstein/g of polymer). Subsequent gas chromatographic analysis showed that the only low molecular weight products isolated were acetophenone and benzaldehyde. Acetophenone would be produced by consecutive type II scissions at the same chromophore, and benzaldehyde by a type I reaction of the polymer or acetophenone followed by hydrogen abstraction. The formation of acetophenone confirms that the type II reaction is responsible for chain scissioning, and the apparent lack of formation of styrene or phenyl vinyl ketone monomers suggests that chain unzipping following a type I reaction is not a favored process.

Triplet Quenching of Polymer Photolysis. 1,3-Cyclooctadiene (COD) was used to study triplet quenching in these polymers. The triplet energy level of COD is not known but has been placed lower than that of acetophenone and propiophenone, since these molecules have been shown to transfer their excitation energy to COD.[17] COD has also been shown to be an effective triplet quencher for aliphatic ketone carbonyls in poly(ethylene-*co*-carbon monoxide).[18]

The results of quenching studies are generally expressed in the form of the Stern–Volmer equation

$$\phi_0/\phi = 1 + k_q\tau[Q]$$

where ϕ_0 and ϕ are the quantum yields for chain scissioning in the absence and presence of the quencher of concentration [Q], respectively, τ is the lifetime of the excited state in the absence of quencher and k_q is the rate constant of energy transfer from donor to acceptor.

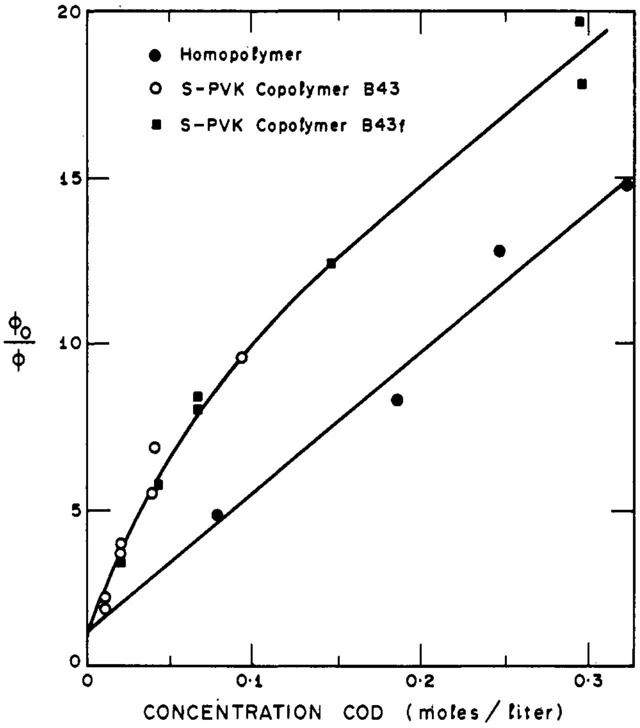

Figure 4. Stern–Volmer plot for quenching of photoscission in poly(PVK) and S–PVK copolymers by COD in benzene solution: (●) poly(PVK), (○) S–PVK copolymer B43, (■) S–PVK copolymer B43f.

TABLE III
QUANTUM YIELD OF CHAIN SCISSIONING OF PPVK; $(\overline{M}_n)_0$ = 67,100

$[(\overline{M}_n)_0/\overline{M}_n] - 1$	ϕ_{cs}
0.296	0.17
0.378	0.28
0.392	0.25
0.520	0.20
0.529	0.23
0.669	0.30
0.812	0.23
1.35	0.30
	Mean 0.245 ± 0.015

Figure 4 depicts such a plot for the homopolymer, and within the experimental error, the expected straight line was attained. At least 93% of the chain scissioning is quenched and therefore probably proceeds from the triplet state. Recently, Wettack, *et al.*,[19] have shown that some quenching of the singlet may also occur at high diene concentrations, but it seems unlikely that this would be a factor at the concentrations used in this work. The slope ($k_q\tau$) has a value of 43 l./mol, with a standard deviation of 1.6. Data for the copolymers B43 and B43f are also shown in Figure 4, and it can be seen that in this case the Stern–Volmer plot does not result in a straight line as is the case for the homopolymer. The experimental values for the two copolymers fall on the same curve, and the initial slope is greater than the slope of the line determined for the homopolymer.

COD probably quenches the triplet state by an exchange rather than a resonance mechanism, since forbidden transitions

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[16] I. Lukac, P. Hrdlovic, Z. Manasek, and D. Bellus, Preprints, IUPAC International Symposium on Macromolecular Chemistry, Vol. 5, Budapest, 1969, p 205.

[17] R. S. H. Liu, *J. Amer. Chem. Soc.*, **89**, 712 (1967).

[18] M. Heskins and J. E. Guillet, *Macromolecules*, **3**, 224 (1970); **1**, 97 (1968).

[19] F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 1793 (1970).

TABLE IV
CHAIN SCISSION QUANTUM YIELD AND LIFETIME OF THE TRIPLET EXCITED STATE

	ϕ_{cs}	τ, sec
Homopolymer	0.245	1.7×10^{-8}
Copolymer	0.176	4.8×10^{-8}

TABLE V
COMPARISON OF KINETIC DATA OF THE POLYMERS AND LOW MOLECULAR WEIGHT PHENYL KETONES

Ketone	ϕ_{II}	k_B, sec^{-1} $\times$ 10^{-7}
$PhCOCH_2CH_2CH_3$	0.35	0.75
$PhCOCH_2CH_2CH_2CH_3$	0.33	14
$PhCOCH_2CH_2CH(CH_3)_2$	0.25	45
$PhCOCH_2CH_2CH_2Ph$	0.49	40
$PhCOCH_2CH_2CH_2COOCH_3$	0.46	1.1
$PhCOCH_2CH_2CH_2CH_2COOCH_3$	0.63	4.0
Poly(PVK)	0.25	5.9
S-PVK copolymer	0.18	2.1

in both the donor and acceptor are involved. Further, in a resonance transfer mechanism, $(\phi_0/\phi) - 1$ would show a dependence on the cube of the COD concentration,[20] and the results of the quenching experiments reported here are not consistent with such a mechanism.

The rate constant for triplet-exchange energy transfer in benzene solution has been shown to be 0.5×10^{10} l./(mol sec) for small molecules.[21] Heskins and Guillet have shown that the ratio k_D/k_q (where k_D is the rate constant for diffusion) remained virtually unchanged when the fluorescence of naphthalene was quenched by 6-undecanone or by a copolymer of ethylene and carbon monoxide.[18]

From these considerations, a value of k_q of 0.25×10^{10} l./(mol sec) may be estimated if the transfer is sufficiently exothermic. Reversible energy transfer which occurs when the (0–0) energy levels of the donor and acceptor are close was ruled out because $k_q\tau$ was found to be independent of polymer (carbonyl) concentration. From this value, and the slope of the Stern–Volmer plot shown in Figure 4, the lifetime of the carbonyl triplet of the homopolymer of PVK was calculated to be 1.7×10^{-8} sec.

The Stern–Volmer plot for the quenching of the copolymer scissioning was not linear. For certain low molecular weight ketones[22] and for poly(ethylene-*co*-carbon monoxide), the nonlinearity was shown to be due to both singlet and triplet participation in the type II and scissioning reactions, respectively. However, low molecular weight phenyl alkyl ketones undergo photoelimination exclusively from the triplet state, and the photoscissioning of the homopolymer also appears to proceed from the triplet state as judged by the linearity of the plot in Figure 4. We therefore suggest the following explanation for this behavior.

In the PVK–styrene copolymers there will be distribution of sequences of various lengths of PVK units rather than PVK units isolated entirely by styrene units. If there is a difference in triplet lifetime between isolated and sequential phenyl vinyl ketone units, this would lead to a nonlinear Stern–Volmer plot. Such a difference might be due to delocalization of the excitation energy (or excimer formation) when the PVK units are part of a sequence.

The initial slope of the Stern–Volmer plot for the copolymers in Figure 4 is considerably greater than the slope of the plot for the homopolymer, suggesting that the triplet lifetime of the isolated PVK units might be longer than when they occur in sequences. (Alternatively, the lifetime might remain constant, but the efficiency of quenching increase.)

In a copolymer of this composition, we can calculate from simple probability considerations that 97.5% of the PVK units are isolated from each other by styrene units, whereas 2.5% of the PVK groups are in dyads, triads, and higher order sequences. The solid line through the copolymer points in Figure 4 is the theoretical relation expected from a system containing 97.5% of units having a half-life of 4.8×10^{-8} sec and the remainder an excited-state lifetime of 0.12×10^{-8} sec, the former value being that calculated from the initial slope of the curve and the latter a value selected to give the best fit to the experimental data. In view of the assumptions and experimental errors involved, the agreement between experiment and theory may well be fortuitous, but it does indicate that an argument of this kind is not inconsistent with the experimental results observed. The values of lifetimes and quantum yields from initial slopes for the homopolymer and copolymers are given in Table IV.

The lifetimes are short, which explains why oxygen does not appear to affect the quantum yield of chain scissioning. The fact that the quantum yields shown in Table V bear no direct relationship with the lifetimes $(1/k_B)$ of the triplet states implies that the quantum yield is not controlled by other processes competing with the scissioning reaction from the triplet state. This fact supports the biradical mechanism as applied to the type II reaction by Wagner and Hammond[23] and Wagner[24] whereby biradical reversal and the type II elimination reaction compete for the biradical species formed from the triplet state with a quantum yield close to unity.

However, other authors[25] have assumed that implicit in this mechanism, the quantum yield and lifetime do not change with increasing chain length. The fact has been shown for the linear aryl alkyl ketones.[11] However, quantum yield has been shown to depend on chain length for both the symmetrical and methyl *n*-alkyl[9,10] ketones.

In Table V is a list of data obtained for low molecular weight phenyl alkyl ketones obtained by Wagner and Kemppainen,[26] including our results for the polymer systems. The values for k_B of the polymers fall within the range of values cited for the phenyl ketones. However, the reactivity of the polymeric ketones (k_B) is less than those obtained for the low molecular weight ketones whose γ-hydrogen is tertiary or whose secondary γ-hydrogen is on a carbon α to a phenyl group.

The decrease in reactivity of the polymeric ketones is probably a measure of the stiffness of these polymer chains. That is, the ease of formation of the cyclic intermediate, rather than the ease of removal of the γ-hydrogen may be lifetime controlling. This was previously suggested as an explanation for the decrease in type II quantum yields of alkyl ketones as the chain length increased.[10]

Acknowledgment. This work was supported by the National Research Council of Canada. We would also like to thank Brian McAneney for his assistance in running the gel permeation chromatograph.

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(20) J. C. W. Chien and W. P. Conner, *J. Amer. Chem. Soc.*, **90**, 1001 (1968).

(21) W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966).

(22) N. C. Yang and S. P. Elliot, *ibid.*, **90**, 4194 (1968).

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

(24) P. J. Wagner, *ibid.*, **89**, 5715 (1967).

(25) C. H. Nicol and J. G. Calvert, **89**, 1795 (1967).

(26) P. J. Wagner and A. E. Kemppainen, *ibid.*, **90**, 5896 (1968).