(13) M. W. Tembold and H. E. A. Kramer, *J. Soc. Dyers Colour.*, **94**, 12 (1978).
(14) V. B. Ivanov and V. Ya. Shlyapintokh, *J. Polym. Sci.*, **16**, 899 (1978).
(15) A. Zweig and W. A. Henderson, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 717 (1975).
(16) H. Kautsky, *Trans. Faraday Soc.*, **35**, 216 (1939).
(17) C. S. Foote and J. W. Peters, *J. Am. Chem. Soc.*, **93**, 3795 (1971).
(18) C. S. Foote and J. W. Peters, *XXIII Int. Congr. Pure Appl. Chem., Spec. Lect. IV*, 129 (1971).
(19) M. Cassagrande, G. Gennari, and G. Cauzzo, *Gazz. Chim. Ital.*, **104**, 1251 (1974).
(20) J. N. Demas, D. Diemente, and E. W. Harris, *J. Am. Chem. Soc.*, **95**, 6864 (1973).
(21) J. N. Demas, R. P. McBride, and E. W. Harris, *J. Phys. Chem.*, **80**, 2248 (1976).
(22) J. N. Demas, E. W. Harris, and R. P. McBride, *J. Am. Chem. Soc.*, **99**, 3547 (1977).
(23) For oxygen-saturated CH_3OH, typical values are $k_3(O_2) \approx 10^7$ and $k_4 \approx 10–10^4$ s^{-1}.[2]
(24) K. Gollnick, T. Franken, G. Schade, and G. Dorhofer, *Ann. N.Y. Acad. Sci.*, **171**, 89 (1970).
(25) M. Nemoto, H. Kokobun, and M. Koisumi, *Bull. Chem. Soc. Jpn.*, **42**, 1223 (1969).
(26) C. E. Rogers in "Engineering Design for Plastics", E. Baer, Ed., Reinhold, New York, 1964, pp 609ff.
(27) J. Brandrup and E. H. Immergut, Eds., "Polymer Handbook", Wiley-Interscience, New York, 1966.
(28) N. J. Turro, M. F. Chow, and M. A. Balustein, *J. Am. Chem. Soc.*, **100**, 7111 (1978).
(29) K. J. Yautsey and L. I. Grossweiner, *Photochem. Photobiol.*, **6**, 721 (1967).
(30) V. S. Srinivasan, D. Podolsk, N. J. Westrick, and D. C. Neckers, *J. Am. Chem. Soc.*, **100**, 6513 (1978).
(31) J. S. Winterle, D. S. Kliger, and G. S. Hammond, *J. Am. Chem. Soc.*, **98**, 3719 (1976).
(32) E. F. Lytle and D. M. Hercules, *Photochem. Photobiol.*, **13**, 123 (1971).
(33) G. Sprintschnik, H. W. Sprintschnik, P. Kirsch, and D. G. Whitten, *J. Am. Chem. Soc.*, **99**, 4947 (1977).
(34) J. G. Calvert and J. N. Pitts, "Photochemistry", Wiley, New York, 1967, pp 783-6.
(35) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
(36) Hanovia Lamp Division, Canrad Precision Industries, Inc., Newark, NJ.
(37) D. Swern in "Organic Peroxides", Vol. 1, D. Swern, Ed., Wiley, New York, 1970, p 498.
(38) Using known values for polymer permeability constants, we calculated that the rate of oxygen transport halfway into a PVC film (2.6×10^{-2} mm thick; 2 mm^2 area) at 30 °C and 2-torr O_2 pressure is 1.9×10^{-12} mol s^{-1}, while under the same conditions for vinyl acetate–vinyl chloride copolymer it is 3.8×10^{-11} mol s^{-1}.
(39) Bourdon et al.[11] and Turro et al.[28] showed that $^1O_2$ can diffuse into polymer films only 500 Å (5×10^{-5} mm) before being quenched.

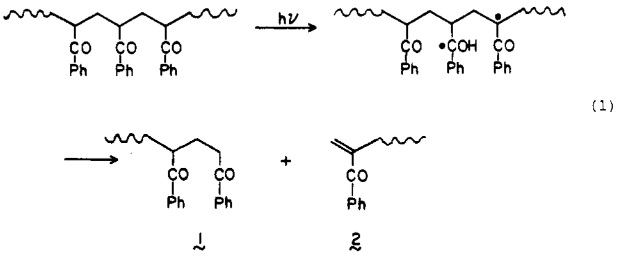
Photochemistry of Polymers and Copolymers of Phenyl Vinyl Ketone and *o*-Tolyl Vinyl Ketone

J. P. Bays, M. V. Encinas, and J. C. Scaiano*[1]

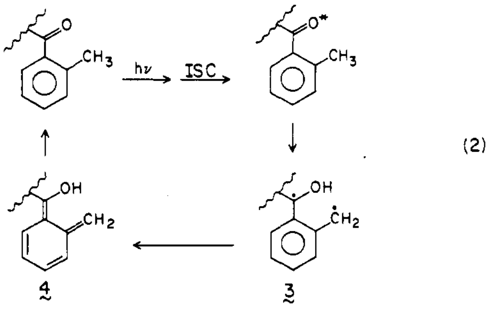
Radiation Laboratory,[2] University of Notre Dame, Notre Dame, Indiana 46556.
Received July 11, 1979

ABSTRACT: Energy migration plays an important role in the photochemistry of polymers containing phenyl vinyl ketone and *o*-tolyl vinyl ketone units. The average "residence time" of the triplet excitation in any given chromophore is in the neighborhood of 30 ps. Triplet lifetimes are estimated as 55 ns for PPVK and 2 ns for PTVK and are intermediate for all the copolymers. Biradical lifetimes are 65 ns for PPVK and 200 ns for PTVK, reflecting the longer lifetime of the biradicals derived from the *o*-methylbenzoyl group. Photoenolization of the *o*-tolyl vinyl ketone moieties provides an energy sink, reducing the degree of photodegration. For example, a copolymer of phenyl vinyl ketone and *o*-tolyl vinyl ketone containing 3% of the latter undergoes only 54% of the degradation undergone by PPVK.

The Norrish type II photofragmentation is an important process in polymer photochemistry.[3,4] The reaction can take place in almost all polymers containing carbonyl groups, including some like polystyrene and polyethylene in which the carbonyl chromophores are incorporated as a result of oxidative processes which are common during polymerization, processing, and purification.[5] Poly(phenyl vinyl ketone), PPVK, is a good model for the Norrish type II process in macromolecules, and its photodegradation (reaction 1) has been the subject of several studies.[4,6-11]



One way in which the energy can be channeled toward nondegradative processes is by providing an alternative reaction path for the excited carbonyl triplet, such that it will essentially behave as a mode of radiationless deactivation. In a recent preliminary communication[12] from this laboratory we have shown that photoenolizations in high polymers can be used to reduce, or prevent, photodegradation. For example, poly(*o*-tolyl vinyl ketone) is a photostable polymer; we have attributed this stability to the sequence of processes illustrated in reaction 2.



The behavior of copolymers of phenyl vinyl ketone and *o*-tolyl vinyl ketone, CoPT, can be expected to be controlled by the relative rates of the various possible photoprocesses, as well as by the possibility of energy migra-

0024-9297/80/2213-0815$01.00/0

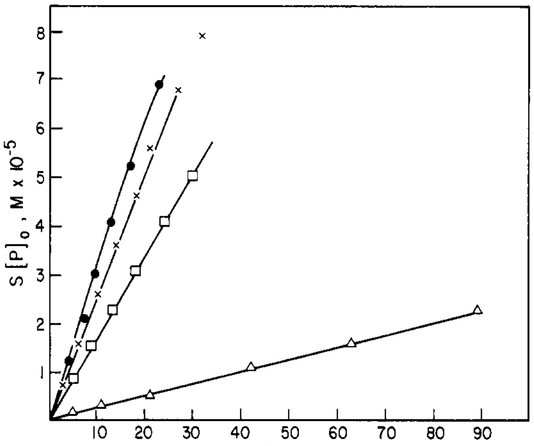


Figure 1. Progress of the photodegradation as a function of time for PPVK (●), CoPT(1) (×), CoPT(3) (□), and CoPT(11) (△). PTVK was stable under the same irradiation conditions for periods of over 300 min.

tion within the polymer. For example, if no energy migration took place, the quantum yield of photodegradation of a given CoPT would be controlled solely by the relative abundance of phenyl and *o*-tolyl groups. In this paper we show that this is not the case and that energy migration is important in controlling the behavior of several CoPT upon UV irradiation.

The results reported herein are from quantum yield studies using viscometric techniques and the examination of transient phenomena using nanosecond laser flash photolysis techniques.

Results

This section is divided according to the experimental technique used. All experiments were carried out under oxygen-free conditions.

Quantum Yield Studies. The progress of the photodegradation was monitored by following the change in viscosity upon irradiation. The quantum yield of photofragmentation, ϕ_{II}, is given by eq 3,[6] where S is the number

$$\phi_{II} = S[P]_0/I_0t \qquad (3)$$

of main-chain scissions per original macromolecule, $[P]_0$ is the initial molar polymer concentration ($[P]_0 = 10c/M_0$), I_0 is the light intensity (in einstein L^{-1} s^{-1}), and t is the time. The number of chain scissions, S, was evaluated according to eq 4, where M is the molecular mass, $[\eta]$ is

$$S = M_0/M - 1 = ([\eta]_0/[\eta])^{1/\alpha} - 1 \qquad (4)$$

the intrinsic viscosity, α is a constant which equals 0.84 for PPVK in benzene, and the zero subscript indicates an initial value.[6] The intrinsic viscosity and the molecular mass, M, were obtained from the specific viscosity, η_{sp}, according to eq 5 and 6. K is Huggins constant (0.465 for

$$\eta_{sp}/c = [\eta] + Kc[\eta]^2 \qquad (5)$$

$$[\eta] = K'M^{\alpha} \qquad (6)$$

PPVK in benzene at 30 °C), K' is a constant equal to 2.82 × 10^{-5} under the same conditions,[6] and c is the polymer concentration in g/100 mL.[13] We have assumed that the same constants could be used for CoPT as for PPVK; this approximation can be expected to be a good one since the copolymers used contained 89% or more phenyl vinyl ketone moieties. In the case of PTVK it is not strictly necessary to use any constants because the polymer is photostable.

Table I[a]

polymer	ϕ_{II}	$k_q\tau_T$[b]	τ_T[c]	τ_B[c]
PPVK	0.24	130	55	65
CoPT(1)[18]	0.194	110	46	75
CoPT(3)[18]	0.130	75	31	160
CoPT(11)[18]	0.020	38	16	250
PTVK	<10^{-3}	4	2	200
PPVK (predegraded)[d]		40	17	

[a] All values in benzene solvent. The temperature is 30 °C for ϕ_{II} and 22 °C for all other parameters. [b] In M^{-1}. [c] In nanoseconds. [d] Subjected to prolonged irradiation before the experiment.

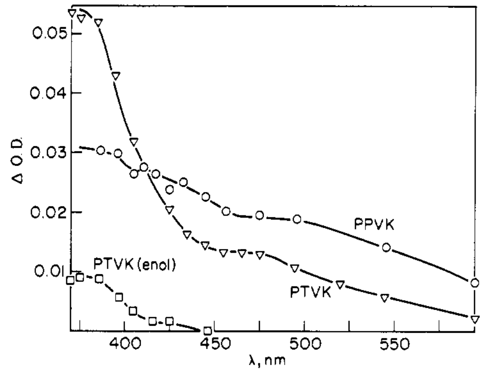


Figure 2. Transient spectra obtained 30–50 ns after the pulse for PPVK (○) and PTVK (▽) and 1 μs later for the enol of PTVK (□).

All measurements are based on initial rates because at higher conversions the presence of unsaturated groups (see reaction 1) causes a decrease in both the triplet lifetime and the quantum yield ϕ_{II}.[15] Figure 1 shows plots of the product $S[P]_0$ vs. time for experiments where $I_0 \sim 2.2 \times 10^{-7}$ einstein L^{-1} s^{-1}. The quantum yields derived from these data have been included in Table I.

In the case of PTVK we have observed that, if the light intensity is increased by a factor of 20–50, the molecular weight increases slightly, presumably as a result of cross-linking which might involve reactions of biradicals and photoenols.

Laser Flash Photolysis. The samples were excited with the pulses (337.1 nm, 8 ns, 3 mJ) from a nitrogen laser, and the resulting transient absorptions were monitored by using a detection system with a nanosecond response. Figure 2 shows the transient spectra obtained 30–50 ns after the excitation pulse for the two homopolymers. The spectrum of CoPT(1) was a mixture of the two shown, while the spectra of CoPT(3) and CoPT(11) were quite similar to the one determined for PTVK. Figure 2 also includes the spectrum of the photoenol from PTVK determined 1 μs after the laser pulse. Special care was taken to ensure that all the data was obtained with fresh samples, i.e., samples which had not been subjected to considerable degradation; whenever necessary, a flow system was used. The differences between the spectrum for PPVK in Figure 2 and that reported earlier by Faure et al.[9b] with which our earlier experiments agreed[10] should be attributed to conversion problems (vide infra).

Triplet lifetimes can be derived from quenching experiments by using 1-methylnaphthalene as a triplet energy acceptor and monitoring (415 nm) the transient absorptions due to the triplet state of the acceptor produced via energy transfer. Reactions 7–9 show the relevant sequence of processes.

$$P^* \xrightarrow{\tau_T} \text{decay} \qquad (7)$$

$$P^* + N \xrightarrow{k_q} P + N^* \qquad (8)$$

$$N^* \xrightarrow{\tau_N} \text{decay} \qquad (9)$$

The asterisk denotes a triplet state, P stands for polymer, and N represents 1-methylnaphthalene. The lifetime of triplet 1-methylnaphthalene, τ_N, is considerably longer than that of the polymer triplet, τ_T, making these measurements quite easy. The values of $k_q\tau_T$ can be derived from these experiments according to eq 10.

$$1/\phi_N = 1 + 1/k_q\tau_T[N] \qquad (10a)$$

$$1/A_N = a + a/k_q\tau_T[N] \qquad (10b)$$

ϕ_N and A_N are the quantum yield and absorbance corresponding to the triplet state of 1-methylnaphthalene. In fact, (10b) is a more convenient equation, since it is directly based on the experimentaly measured transient absorbance due to the 1-methylnaphthalene triplet, A_N, and an arbitrary constant a. The values of $k_q\tau_T$ (see Table I) are obtained from the intercept-to-slope ratio according to eq 10b (Figure 3). Changes in the intercept (see Figure 3) can result from changes in the experimental conditions, since neither the exact laser power nor the overlap between monitoring and excitation beams is exactly reproducible on a day-to-day basis.

In order to obtain triplet lifetimes from the $k_q\tau_T$ values listed in Table I, it is necessary to estimate the value of k_q. In the case of methyl methacrylate–phenyl vinyl ketone copolymers we have determined $k_q = 2.4 \times 10^9$ M^{-1} s^{-1} at room temperature,[16] and the values of τ_T given in Table I are based on this figure. The use of a k_q value obtained with a polymer where energy migration is unimportant is not strictly correct since energy hopping could lead to an increase in the effective size of the donor segment in the polymer. We feel that the error introduced in these systems will not exceed a factor of 2 as a result of the quadratic dependence of the distance travelled (or chromophores visited) with the number of hops.[17]

We have also examined the lifetimes of the biradicals involved in the photofragmentation and/or photoenolization of the polymers under study. For all the copolymers the signals observed should be attributed to a mixture of the biradicals involved in reactions 1 and 2. A rigorous kinetic analysis would predict that two species decaying with different lifetimes should not lead to simple exponential decays. In practice, the experimental time profiles can be fitted by following a simple first-order approach; further elaboration would be mere speculation.

With the exception of PPVK and CoPT(1), the measurement of biradical lifetimes is straightforward as a result of the comparatively short triplet lifetimes ($\tau_B > \tau_T$), and Figure 4 illustrates a typical decay trace for PTVK and the corresponding first-order plot.

In the case of PPVK and CoPT(1) the triplet and biradical lifetimes are comparable, and the corresponding transient absorptions, while somewhat different, extend over the same spectral region. In other words, the two signals overlap in both wavelength and time. There are two ways in which the biradical lifetimes can be determined, and both are based on the idea of shortening the triplet lifetime at the expense of some decrease in the signal intensity: (i) Addition of a diene, e.g., *trans*-1,3-pentadiene, results in the quenching of the triplet state and as a result allows the tuning of τ_T to a conveniently short value.[20] The effective lifetime, τ_T', after tuning is given by eq 11, where [Q] is the quencher concentration.

$$1/\tau_T' = 1/\tau_T + k_q[Q] \qquad (11)$$

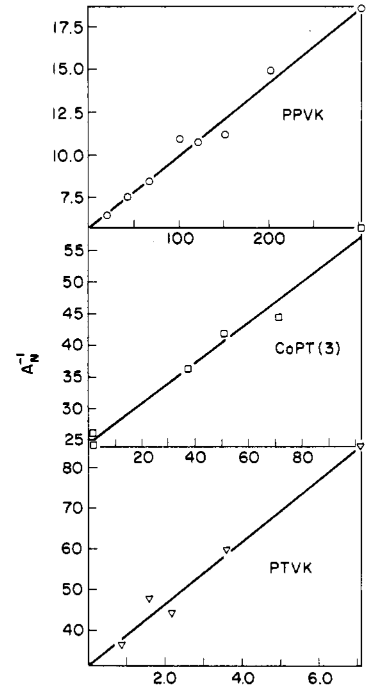


Figure 3. Representative plots (according to eq 10b) leading to the evaluation of $k_q\tau_T$ for PPVK (top), CoPT(3) (center), and PTVK (bottom).

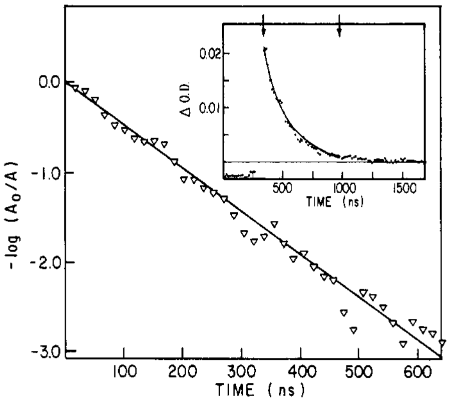


Figure 4. Decay trace for the biradical from PTVK as monitored at 395 nm (insert) and corresponding first-order plot. The two arrows in the insert indicate the section of the trace used to evaluate the kinetics. The difference between the original and final base line reflects the absorbance due to the photoenol (λ 395 nm).

(ii) Partially degraded samples of PPVK have shorter triplet lifetimes than fresh, carefully handled ones. The difference is the result of quenching by unsaturated end groups which result from efficient energy hopping between carbonyl chromophores.[15] In partially degraded samples of PPVK we have measured $k_q\tau_T$ values as low as 40 M^{-1} (using the 1-methylnaphthalene technique). In these partially degraded samples the observable signals correspond almost exclusively to the biradical (in particular at λ >400 nm). This condition was fortuitously met in our earlier studies,[10] and allowed the straightforward study of biradical processes. Presumably, the same arguments are applicable to Faure's data,[9b] since the spectrum reported by his group is clearly that of the biradical.

τ_B's for PPVK and CoPT(1) were measured by "tuning" the corresponding triplet lifetimes to 10 ns or less (i.e., [diene] ≥ 0.04 M). Under these conditions the lifetimes measured are those of the biradical, as shown by the fact that the value of τ_B is insensitive to further addition of

Table II
Effect of *o*-Methylbenzoyl Groups on the Yield of Degradation

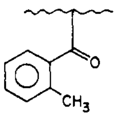
polymer	% degradation	% prevented
PPVK	100	0
CoPT(1)[18]	81	19
CoPT(3)[18]	54	46
CoPT(11)[18]	8	92
PTVK	0	100

diene. We note that the measurement of biradical lifetimes depends upon the triplet lifetime being short but does not require the knowledge of the exact value of τ_T.[20,21]

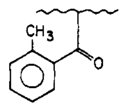
Discussion

Table II shows the relative yield of degradation of PPVK observed for each of the copolymers. The fact that *o*-methylbenzoyl groups prevent degradation far in excess of their relative abundance is ample evidence that energy migration within the polymer must be an important process.

The quenching plots obtained with 1-methylnaphthalene for the copolymers [see Figure 3 for CoPT(3)] were all reasonably linear, indicating that the triplet states of the two chromophores present in the macromolecule are not distinguishable by our technique. The presence of only one triplet in each polymer sample can be taken as indicative of fast energy migration, ideally of excitation equilibration throughout the polymer molecule. We note that if energy migration was not an important process, the plots in Figure 3 would lead to regions with different slopes, one for each triplet state. In fact, one should expect two triplets from the *o*-methylbenzoyl group, i.e., the syn and anti conformers:[22]



syn



anti

Conformational equilibration is a relatively slow process and one cannot expect it to be achieved within the short triplet lifetime of PTVK or copolymers rich in *o*-tolyl vinyl ketone.[22] The detection of only one triplet in PTVK can be attributed to fast energy migration which effectively leads to energy hopping through anti conformations until the energy sink, the syn conformation, is reached; i.e., the anti conformation plays only a passive role in the process.

The quantum yields of photodegradation of copolymers are expected to be controlled by the relative abundance of phenyl and *o*-tolyl groups, by the rate of energy hopping (k_H), by the rate of intramolecular hydrogen abstraction for the type II process (k_{II}), and by the rate of enolization (k_E). Under conditions of complete equilibration relation 12 will hold, where f_T is the fraction of tolyl groups.[23] This

$$k_H \gg k_E/f_T \tag{12}$$

relation is simply based on the idea that in order to achieve energy equilibration the rate of hopping must exceed the rate of the fastest decay process, i.e., the enolization of the syn triplet conformer. The presence of f_T in (12) introduces a dependence with the average distance between enolizable chromophores. For example, for CoPT(1) the rate of hopping would have to exceed by 100 times the rate of enolization.[24] If equilibration is achieved, the yield of photodegradation would be given by eq 13, where N_T and

$$\frac{\phi_{II}}{\phi_{II}(\mathrm{PPVK})} = \frac{k_{II}}{k_{II} + N_T k_E / N_P} \tag{13}$$

N_P are the number of *o*-tolyl and phenyl chromophores, respectively, and $\phi_{II}(\mathrm{PPVK})$ is the quantum yield of photodegradation for PPVK. According to eq 13, ϕ_{II}^{-1} should depend linearly on the N_T/N_P ratio, eq 14.

$$\frac{\phi_{II}(\mathrm{PPVK})}{\phi_{II}} = 1 + \left(\frac{N_T}{N_P}\right)\left(\frac{k_E}{k_{II}}\right) \tag{14}$$

The quantum yield data given in Table I does not follow the linear dependence predicted by eq 14; i.e., it does not seem to meet the condition of complete triplet excitation energy equilibration.

On the other extreme, if the decrease in yields was the result of a process kinetically controlled by k_H, then the theory of random walk for a one-dimensional lattice[15,18] would predict a quadratic dependence of ϕ_{II}^{-1} with N_T/N_P, i.e.

$$\phi_{II}^{-1} \propto (N_T/N_P)^2 \tag{15}$$

In practice, neither eq 15 nor eq 14 represents adequately the dependence of the quantum yield with polymer composition. An exponent of ~1.6 in eq 15, rather than 2, seems to give the best correlation.

We interpret this result as meaning that, while energy migration is an important process and energy equilibration is *approached*, full equilibration is not achieved. The system cannot be very far from equilibration, since this would lead to significant curvature of the plots in Figure 3. In other words the left and right terms in eq 12 are probably of the same order of magnitude. The rate of decay of triplet PTVK is 0.5×10^9 s^{-1}. This corresponds to an overall process involving migration toward the syn conformation and decay from this geometry. If we assume that for the average copolymer $f_T \sim 0.03$, the k_H will be of the order of $\sim 3 \times 10^{10}$ s^{-1}; that is, the average residence time of the energy in each chromophore must be of the order of 30 ps. This should only be regarded as an "order of magnitude" calculation rather than a rigorous treatment. We note that triplet energy migration in PVK–TVK copolymers involves four different migration steps, depending on the nature of the donor and acceptor moieties; i.e., PVK* → PVK, PVK* → TVK, TVK* → TVK, and TVK* → PVK. The first step indicated (PVK* → PVK) is likely to occur with a rate similar to that in the homopolymer, i.e., $\sim 10^{12}$ s^{-1},[15] and the average residence time indicated above is likely to reflect a slower rate for one or both transfers between nonidentical units.

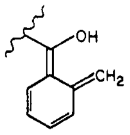
We come now to the relative values of τ_T and τ_B and their importance in determining the type of transient species detected. The presence of *o*-methylbenzoyl chromophores in the polymers causes an increase in the biradical lifetime and a decrease in the triplet lifetime. Even 1% substitution is enough to make the biradical lifetime almost twice the triplet lifetime, and 3% makes the biradical lifetime five times longer than that of the triplet state. As a result, the experimental traces for CoPT(3), CoPT(11), and PTVK are those for the biradicals. In CoPT(3) there is some mixture of **3** and type II transient biradicals, but for CoPT(11) and PTVK the signal is simply that of the biradical involved in the photoenolization process, **3**. Examination of Table II shows that in CoPT(3) one should detect a roughly equimolar mixture of the two biradicals immediately after triplet decay.

In the case of PPVK the trasient spectrum observed corresponds to a mixture of signals from the triplet state and the biradical. Our earlier report[10] on the study of biradical processes in PPVK using laser flash techniques was correct as a result of the rather fortunate use of a polymer sample which contained some unsaturated (see 2) end groups which led to the shortening of the triplet lifetime.

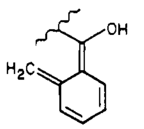
The biradical lifetimes are longer for those derived from *o*-methylbenzoyl chromophores, as could be anticipated from earlier studies in small molecules.[25,26] We find it somewhat surprising that the value of τ_B in CoPT(11) is somewhat longer than that for PTVK. Presumably, the environment plays a role in controlling the lifetime, suggesting that biradicals derived from isolated (or rather surrounded by PVK moieties) *o*-methylbenzoyl chromophores have longer lifetimes than sequential ones (PTVK). The reasons for this difference are as yet unclear.

Biradical decay traces do not return to the original (prepulse) base line in the time scale of the biradical decay, indicating the presence of a slow-decaying residual absorbance. The effect is more important in PTVK than in PPVK, where enol absorption can be neglected in the spectral range examined, with intermediate behavior for the copolymers. We attribute this residual absorbance to the enols, i.e., species 4 in reaction 2, for which the transient spectrum is given in Figure 2. We note that the type II photofragmentation also leads to a ketone in the enol form, as has been established by several research groups.[27]

Two isomeric enols are expected in the case of PTVK, **4*Z*** and **4*E***.



4Z



4E

Previous research[26] in small molecules has shown that *Z* enols are very short-lived in nonpolar media, as is the case in our experiments. Therefore, we conclude that the residual signals observed are due to **4*E***, which is also likely to be involved in the slight increase in molecular weight observed upon steady high-intensity irradiation.

Finally, we come to the question of the potential applications of the *o*-methylbenzoyl chromophore in order to prevent polymer photofragmentation. The last column in Table II shows the fraction of fragmentation prevented by the *o*-methylbenzoyl chromophore in each polymer. For example, 3% substitution decreases the photodegradation by ca. 50%. One can anticipate even more effective stabilizations in other systems where the reaction leading to degradation (i.e., k_{II}) would be slower, as would be the case for secondary, rather than tertiary, abstractable hydrogens. Energy hopping is clearly an important process and one could expect a different effectiveness in systems with nonsequential chromophores; this possibility is currently being examined.

Conclusion

o-Methylbenzoyl groups stabilize polymers which otherwise would undergo the Norrish type II photocleavage. The effect is due to the photoenolization of this chromophore, a process which competes favorably with the photofragmentation. Laser flash photolysis confirms the mechanism suggested above, as reflected by the decrease in overall triplet lifetime resulting from incorporation of *o*-methylbenzoyl groups, as well as by the spectroscopic properties of the resulting biradical, which closely resemble those for the biradical from *o*-methylacetophenone.

Energy migration is shown to be an important process, and an analysis of two extreme models, one requiring full triplet excitation equilibration and the other where the process is determined by the one-dimensional diffusion of the triplet excitation, shows that the average "residence time" of the energy in any given chromophore must be in the neighborhood of 30 ps and is consistent with our earlier report of an upper limit of 1 ns in this polymer[12] as well as with similar studies in 1,5-diaryl 1,5-diketones[21] and the homopolymer PPVK.[15]

Experimental Section

Monomer Preparation. Phenyl vinyl ketone was prepared from β-chloropropiophenone by dehydrochlorination with potassium acetate according to literature methods.[28] *o*-Tolyl vinyl ketone was synthesized by oxidation of *o*-tolyl vinyl alcohol with CrO_3, according to a literature procedure.[29]

Materials. β-Chloropropiophenone, *o*-methylacetophenone, azobis(isobutyronitrile) (AIBN), 1-methylnaphthalene, and *trans*-1,3-pentadiene are all Aldrich products.

Benzene (Aldrich, Gold Label) was used as received.

Polymer Preparation. All polymerizations were initiated with AIBN and were typically carried out at 50 °C in the dark and under nitrogen. The corresponding starting monomer mixture was diluted (1/3) with benzene, and conversions never exceeded 15%. The polymers were precipitated with methanol, separated, and redissolved in benzene. This process was repeated 6–8 times; the last benzene solution was then freeze-dried. Special precautions were taken to carry out all these operations as well as the preparation of polymer solutions in the dark. Low-actinic glassware was used whenever available. These precautions are particularly important in the case of the highly photosensitive PPVK. The molecular weights of the samples used were usually in the neighborhood of 2×10^5.

Determination of Copolymer Compositions. The relative abundance of the two monomers in the copolymers was determined from a study of their ^{13}C NMR spectra and a comparison with those for the homopolymers, PPVK and PTVK. The spectra were recorded on an FT Varian XL-100 instrument. The solvent was Cl_3CD, and Me_4Si was used as a reference. For PPVK we observed signals at δ 34.82 (CH_2, backbone), 41.30 (CH, backbone), 128.1, 132.8, 136.4 (aromatic), and 202.2 (carbonyl). For PTVK, we obtained δ 21.29 (*o*-CH_3), 34.8 (CH_2, backbone), 44.19 (CH, backbone), 125.6, 128.47, 136.1, and 138.1 (aromatic), and 205.4 (carbonyl). The shifts for the PVK and TVK in the copolymers were essentially identical with the positions in the homopolymers. The compositions given in Table I are based on a study of the relative intensity of the signals from the two moieties and comparison with the homopolymer spectra. The carbonyl signal was quite useful for this purpose. We found that the experimental compositions are quite close to that of the monomer mixture used in the preparation. For example CoPT(11) was obtained from the polymerization of a 10:90 mixture of TVK and PVK.

Quantum Yields. All irradiations were carried out in samples deaerated with oxygen-free nitrogen; they were contained in a modified viscosimeter which allowed us to deaerate, irradiate, and measure the viscosity without any need for sample transfers. The complete unit was immersed in a constant-temperature bath at 30.00 ± 0.02 °C. Flow times were measured with a Wescan Model 221 automatic viscosity timer. Averages of 5–10 measurements led to standard deviations of the order of 0.01–0.03 s for flow times between 70 and 250 s. The light source was a combination of a Bausch & Lomb 200-W high-pressure mercury lamp and a high-intensity monochromator. Irradiations were carried out at 366 nm. Pyrex windows and glassware were used throughout.

Actinometries were carried out by monitoring the photofragmentation of valerophenone in benzene, for which ϕ(acetophenone) = 0.30.[30] Acetophenone was measured with a gas chromatograph using a column of 5% DC-11 silicone oil on Chromosorb W and a Beckman GC-5 instrument equipped with flame ionization detectors. Undecane was used as an internal standard.

Laser Flash Photolysis. The samples were excited with the pulses (337.1 nm, ~8 ns, 3 mJ) from a Molectron UV-400 nitrogen laser. The monitoring source was a pulsed Eimac 150-W xenon lamp. The detection system consisted of a Bausch & Lomb high-intensity monochromator and an RCA-4840 photomultiplier tube with four dynodes connected. The signals were terminated into 93 Ω and into a Tektronix R7912 transient digitizer with a local 4K memory. The signals were then transmitted to a PDP 11/55 multiuser computer system which controlled the experiment, averaged the signals, processed the data, and provided mass-storage devices.

The samples were contained in Suprasil cells with 3-mm optical paths or in a flow system with the same optical path whenever the samples had to be subjected to many laser pulses.

Acknowledgment. Thanks are due to D. Schifferl for recording the ^{13}C NMR spectra. J.P.B. acknowledges the use of the facilities from Saint Mary's College, Notre Dame, IN, where part of the experimental work was performed.

References and Notes

(1) To whom correspondence should be addressed at the National Research Council, Division of Chemistry, Ottawa, Canada K1A 0R6

(2) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2030 from the Notre Dame Radiation Laboratory.

(3) E.g.: DeSchryver, F. C.; Smets, G. In "Reactivity, Mechanism and Structure in Polymer Chemistry"; Jenkins, A. D., Ledwith, A., Eds.; Wiley: New York, 1974; Chapter 14.

(4) Ranby, B.; Rabek, J. F. "Photodegradation, Photooxidation and Photostabilization of Polymers"; Wiley: New York, 1975; Chapter 4.

(5) Klöpffer, W. *Eur. Polym. J.* **1975**, *11*, 203.

(6) Lukâk, I.; Hrdlovic, P.; Manâsek, Z.; Bellus, D. *J. Polym. Sci., Polym. Chem. Ed.* **1971**, *9*, 69.

(7) Golemba, F. J.; Guillet, J. E. *Macromolecules* **1972**, *5*, 212. Somersall, A. C.; Dan, E.; Guillet, J. E. *Ibid.* **1974**, *7*, 233. Dan, E.; Somersall, A. C.; Guillet, J. E. *Ibid.* **1973**, *6*, 228. Dan, E.; Guillet, J. E. *Ibid.* **1973**, *6*, 230.

(8) Kiwi, J.; Schnabel, W. *Macromolecules* **1976**, *9*, 468; **1975**, *8*, 430. Beck, G.; Dobrowolski, G.; Kiwi, J.; Schnabel, W. *Ibid.* **1975**, *8*, 9. Dobrowolski, G.; Kiwi, J.; Schnabel, W. *Eur. Polym. J.* **1976**, *12*, 657. Beck, G.; Kiwi, J.; Lindenau, D.; Schnabel, W. *Ibid.* **1974**, *10*, 1069.

(9) (a) Faure, J.; Fouassier, J.-P.; Lougnot, D.-J. *J. Photochem.* **1976**, *5*, 13. (b) Faure, J.; Fouassier, J.-P.; Lougnot, D.-J.; Salvin, R. *Nouv. J. Chim.* **1977**, *1*, 15. (c) Faure, J. *Pure Appl. Chem.* **1977**, *49*, 487.

(10) Small, Jr., R. D.; Scaiano, J. C. *Macromolecules* **1978**, *11*, 840.

(11) David, C.; Demarteau, W.; Geuskens, G. *Eur. Polym. J.* **1970**, *6*, 1405.

(12) Bays, J. P.; Encinas, M. V.; Scaiano, J. C. *Macromolecules* **1979**, *12*, 384.

(13) The values of K and α have been determined[6] by comparing viscosity measurements with osmotic pressure determinations; therefore values of $\bar{M}_n$[14] are obtained. The calibration was carried out with polymers prepared under the same conditions as ours; even the changes in M were achieved via photodegradation. Therefore the use of eq 6 to monitor degradation is quite reliable.[6]

(14) Van Krevelen, D. W.; Hoftyzer, P. J. "Properties of Polymers"; Elsevier: Amsterdam, 1972; Chapter 1.

(15) Encinas, M. V.; Funabashi, K.; Scaiano, J. C. *Macromolecules* **1979**, *12*, 1167.

(16) Copolymers of methyl methacrylate and phenyl vinyl ketone have relatively long triplet lifetimes when the concentration of ketone groups is low. The value given for k_q was obtained in laser flash experiments in which 2,5-dimethyl-2,4-hexadiene was used as a triplet quencher. Encinas, M. V.; Scaiano, J. C., to be submitted for publication.

(17) That is, the number of hops, $\langle n \rangle$, required to visit N units will be proportional to N^2.[18] One can estimate[18] that for $k_H \sim 3 \times 10^{10}\ s^{-1}$ and an encounter which lasts less than 1 ns, the number of chromophores visited by the excitation during that time will be less than eight. In other words, in any given polymer-quencher encounter the energy will be located within a limited segment of the polymer. We note that in the case of small molecules a value of $k_q = 5 \times 10^9\ M^{-1}\ s^{-1}$ is usually accepted.[19] In any case it should be clear that, strictly speaking, the values of τ_T in Table I should be regarded as upper limits. We are grateful to one of the referees for raising this point.

(18) Montroll, E. W. *J. Phys. Soc. Jpn., Suppl.* **1969**, *26*, 6–10. *J. Math. Phys. (N.Y.)* **1969**, *10*, 753–65.

(19) Wagner, P. J.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 1245–51.

(20) See also: Small, Jr., R. D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4512.

(21) Bays, J. P.; Encinas, M. V.; Small, Jr., R. D.; Scaiano, J. C. *J. Am. Chem. Soc.*, **1980**, *102*, 727.

(22) Wagner, P. J.; Chen, C.-P. *J. Am. Chem. Soc.* **1976**, *98*, 239. Wagner, P. J. *Pure Appl. Chem.* **1977**, *49*, 259.

(23) Perhaps a more accurate expression would include only the fraction of tolyl groups in the syn conformation, rather than f_T. For the purpose of the qualitative discussion given here f_T is a good approximation.

(24) The number in parentheses indicates the percent abundance of tolyl groups in the copolymer.

(25) Small, Jr., R. D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 7713. Das, P. K.; Encinas, M. V.; Small, Jr., R. D.; Scaiano, J. C. *Ibid.* **1979**, *101*, 6965–70.

(26) Haag, R.; Wirz, J.; Wagner, P. J. *Helv. Chim. Acta* **1977**, *60*, 2595.

(27) Scaiano, J. C.; Lissi, E. A.; Encinas, M. V. *Rev. Chem. Interm.* **1978**, *2*, 139 and references therein.

(28) Freedman, H. H.; Mason, J. P.; Medalia, A. I. *J. Org. Chem.* **1958**, *23*, 76.

(29) Thorsett, E. D.; Stermite, F. R.; O'Donnel, C. M. *Synth. Commun.* **1972**, *2*, 375.

(30) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506.