Laser flash photolysis studies on homo- and copolymers of phenylisopropenyl ketone and of pivalophenone in solution

Ikuo Naito*, Ralf Kuhlmann and Wolfram Schnabel
Hahn-Meitner-Institut für Kernforschung Berlin GmbH, D-1000 Berlin 39, W. Germany
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Benzene solutions of poly(phenylisopropenyl ketone) (PPIK), of copolymers of PIK and styrene and of phenyl-t-butyl ketone (pivalophenone) were irradiated with light flashes (duration 25 nsec) at wavelength 347 nm. The spectra observed at the end of the flash were attributed to the triplet state (T–T-spectra). A fraction of the triplets in the polymers was deactivated by T–T annihilation, as evidenced by lifetimes decreasing with increasing absorbed dose rate. Upon extrapolation to zero intensity the following triplet decay rate constants k_T were obtained:

(1.0 ± 0.1)10^7sec^{-1}(PPIK),
(8 ± 1)10^6sec^{-1} (CP–St–PIK–12), (6 ± 1) 10^6 sec^{-1} (CP–St–PIK–3.7),
(3 ± 1)10^6sec^{-1}(CP–St–PIK–1),
(2.5 ± 0.2)10^6sec^{-1}(pivalophenone).

In PPIK and pivalophenone the dominant chemical route of triplet deactivation is α-cleavage. The relatively high k_T value found with PPIK is presumably due to next neighbour interaction. In copolymers with a high content of isolated PIK units type I processes (α-cleavage) become less probable due to weak next neighbour influence. Thus type II processes dominate in copolymers although being slower than type I processes in homo PPIK. The rate constant of the reaction of PIK triplets in homo PPIK with 2-propanol in benzene solution is (2.0 ± 0.2)10^6 l/mol sec, whereas pivalophenone triplets react almost 10 times slower with 2-propanol. The difference is assumed to be due to a rather strong interaction of 2-propanol with ground state as well as with excited pivalophenone.

INTRODUCTION

Flash photolysis studies[1] using light at 347 nm on copolymers of phenyl vinyl ketone (PVK) and methyl methacrylate (MMA), styrene (St) or vinyl acetate (VAc) have shown that the triplet lifetime, τ, depends strongly on the copolymer composition. τ was found to increase steadily with decreasing PVK content. The effect was most strongly pronounced with CP–MMA–PVK, where τ amounted to several μsec at PVK contents less than about 1 mol % (in the case of homo PPVK $\tau \approx 0.1$ μsec).

The essential chemical route of deactivation of triplet excited PVK units is the Norrish type II reaction leading to main chain rupture. The pronounced increase of τ with decreasing PVK content in CP–MMA–PVK samples was, therefore, assumed to be due to the fact that more and more hydrogen atoms in γ-position to the carbonyl group were substituted by methyl groups as the MMA content increased. In the case of copolymers of PVK with styrene τ increased only by a factor of two upon decreasing the PVK content, which might be due to energy migration along the chains being still possible to a certain extent when PVK units are substituted by styrene moieties. On the other hand, nearest neighbour effects might possibly be responsible for longer triplet lifetimes at lower PVK contents.

The present paper reports results of analogous studies with poly(phenylisopropenyl ketone) (PPIK) and with copolymers of PIK and St. Furthermore, results obtained with pivalophenone (phenyl-t-butyl ketone) are reported. We considered pivalophenone a model compound for PPIK. Its photochemistry has been investigated by Lewis and Magyar[2,3] and by Atkins *et al.*[4]. According to their work α-cleavage is occurring upon irradiation of pivalophenone in benzene solution with light at 366 nm leading to the formation of benzaldehyde ($\phi = 0.3$ in the presence of thiol), isobutane and isobutene. The rate constant k_α equal to 1.1×10^7 sec^{-1} was determined by quenching the benzaldehyde yield with naphthalene[3] (assuming $k_q = 5 \times 10^9$ l/mol sec). From time resolved e.s.r. measurements $k_\alpha = 5 \times 10^6$ sec^{-1} was estimated[4]. To the best of our knowledge, the photochemistry of homo-PPIK has not yet been investigated. Main chain rupture according to a Norrish type II process *via* a 6-membered ring intermediate is not possible because there is no H-atom in the γ-position to the carbonyl group. Instead, α-cleavage is expected to occur with a rather high probability. A recent report by Guillet *et al.*[5] concerns studies of copolymers of PIK (and ring substituted PIK) and styrene in 1,2-dichloroethane solution. Upon irradiating CP–PIK–St containing 8.5 mol % PIK with light at 366 nm those authors found a quantum yield for main chain scission of 0.26. It was assumed that main chain scission is occurring *via* a Norrish type II process, since γ-hydrogen atoms are available for excited carbonyl groups if PIK units are separated by styrene moieties.

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* On leave from Kyushu Sangyo University, Fukuoka, Japan.

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Table 1 Characterization of polymer samples

Sample	*MW*	PIK content (mol%)	Polymer concentration of benzene solutions used for irradiation experiments (g/l)
homo PPIK	$\overline{M}_n$: 6×10^3	100	0.2
CP-St-PIK-12	$\overline{M}_w$: 5×10^4	12.0	1.4
CP-St-PIK-3.7	$\overline{M}_w$: 6×10^4	3.7	4.5
CP-St-PIK-1	$\overline{M}_w$: $3,5 \times 10^5$	1.0	16.0

EXPERIMENTAL

Apparatus

Sample solutions were irradiated in rectangular quartz cells with 25 nsec light flashes ($\lambda = 347.1$ nm) from a ruby laser (Korad Model K1QS2) as described before[1]. The optical absorption detection method was applied in order to detect intermediates and to follow their decay. Normal laser operation yielded about 5×10^{16} photons per flash as measured by the potassium ferrioxalate actinometer ($\phi(Fe^{2+}) = 1.20$). Choosing appropriate solute concentrations the optical density was kept as 0.1, corresponding to about 20% absorption of the photolysing light.

Materials

Benzene (Merck, spectroscopy grade) was washed 5 times with concentrated H_2SO_4 and several times with distilled water. It was dried over anhydrous $CaCl_2$ and CaH_2 and finally distilled *via* a splitting tube column (Fischer–Bonn). 2-Propanol (Merck, spectroscopy grade) was treated with anhydrous Na_2SO_4 and refluxed for 10 h over Mg, then distilled via a splitting tube column.

Phenylisopropyl ketone (PIK) was synthesized by a Mannich reaction from propiophenone and paraformaldehyde[8]. The polymerization of PIK was achieved by an ionic mechanism in dioxane solution using n-C_4H_9Li as initiator[9]. The molecular weight of the homo-PPIK was determined by membrane osmometry as $\overline{M}_n = 6 \times 10^3$.

Copolymers of PIK and styrene were prepared by free radical polymerization using AIBN as initiator in benzene solution at 50°C. The total monomer concentration was 4 mol/l. The copolymer composition was determined by elemental analysis and by measuring the optical absorption of the PIK units at $\lambda = 347$ nm ($\epsilon = 60.2$ l/mol cm) and at 320 nm ($\epsilon = 128$ l/mol cm).

Three samples containing 1, 3.7 and 12 mol % PIK were used for these experiments (see *Table 1*).

Pivalophenone(*t*-butyl phenyl ketone) was synthesized as described by Ford *et al.*[10].

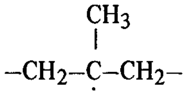
RESULTS

Homo PPIK

Figure 1a shows transient absorption spectra obtained with benzene solutions at room temperature immediately and 700 nsec after the 25 nsec flash. It is seen that the spectrum at $t = 0$ possesses a maximum at about 450 nm which disappears rather rapidly. The decay of the absorption is demonstrated by the oscilloscope traces shown in *Figure 2a*. Above $\lambda = 500$ nm the absorption decreased rapidly to zero, whereas at lower wavelengths a rather long lasting absorption was observed. The absorption at $\lambda > 500$ nm decayed exponentially, as shown in *Figure 3*. The lifetime increased with decreasing incident intensity. An extrapolation to zero intensity yielded $k_T = (1.0 \pm 0.1)\ 10^7\ \text{sec}^{-1}$. The same rate constant was obtained for the decay of the short-lived portion of the transient absorption at lower wavelengths if it was taken into account that the long-lived portion of the transient absorption at lower wavelengths is growing-in simultaneously with the decay of the short-lived transient. The formation of the long-lived transient whose spectrum is shown in *Figure 4* could not be observed directly because of the rather strong absorption of the short-lived species in the wavelength range investigated. The spectrum (see *Figure 4*, curve B) obtained 150 μsec after the flash is assigned to the benzoyl radical, whose absorption spectrum is reported[6] to have a maximum at 275 nm.

From quenching experiments with naphthalene and biphenyl it was inferred that the short-lived absorption is due to triplet excited moieties in PPIK. In the presence of naphthalene or biphenyl (which do not absorb at 347 nm) the formation of the respective *T–T* spectra was observed [λ_{max} at 413 nm (naphthalene) and 370 nm (biphenyl)]. Oscilloscope traces resemble strongly those obtained with pivalophenone shown below (see *Figure 6*). Variation of the quencher concentration (10^{-3} to 10^{-2} mol/l) and a Stern–Volmer treatment of the data yielded rate constants $k_q = (1.5 \pm 1)\ 10^9$ l/mol sec.

It is assumed that the major portion of the long-lived absorption is composed of the spectrum of benzoyl radicals formed by α-cleavage. The corresponding radical



$$-CH_2-\overset{\overset{CH_3}{|}}{\underset{\cdot}{C}}-CH_2-$$

is thought to absorb only very weakly in the wavelength range under investigation. The long-lived absorption was found to decrease with time according to a 2nd order process with a first half-life of about 2 msec.

Oxygen accelerated the rate of decay of the short-lived species. A rate constant $k_{O_2} = (6 \pm 1)\ 10^8$ l/mol sec was estimated.

Upon addition of 2-propanol to benzene solutions of PPIK (up to 6 mol/l) no change of the transient spectrum

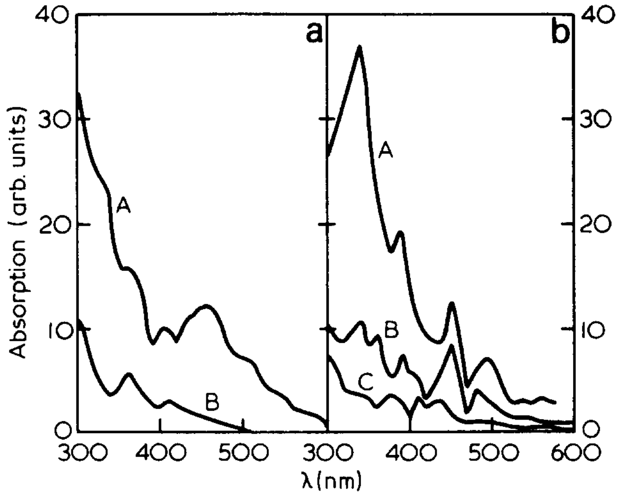


Figure 1 Transient absorption spectra observed A: immediately at the end of a 25 nsec flash ($t = 0$) and at B: 0.7 μsec and C: 10 μsec after the flash, for (a) PPIK in benzene (1.5×10^{-3} base mol/l); (b) pivalophenone in benzene (2.6×10^{-3} mol/l)

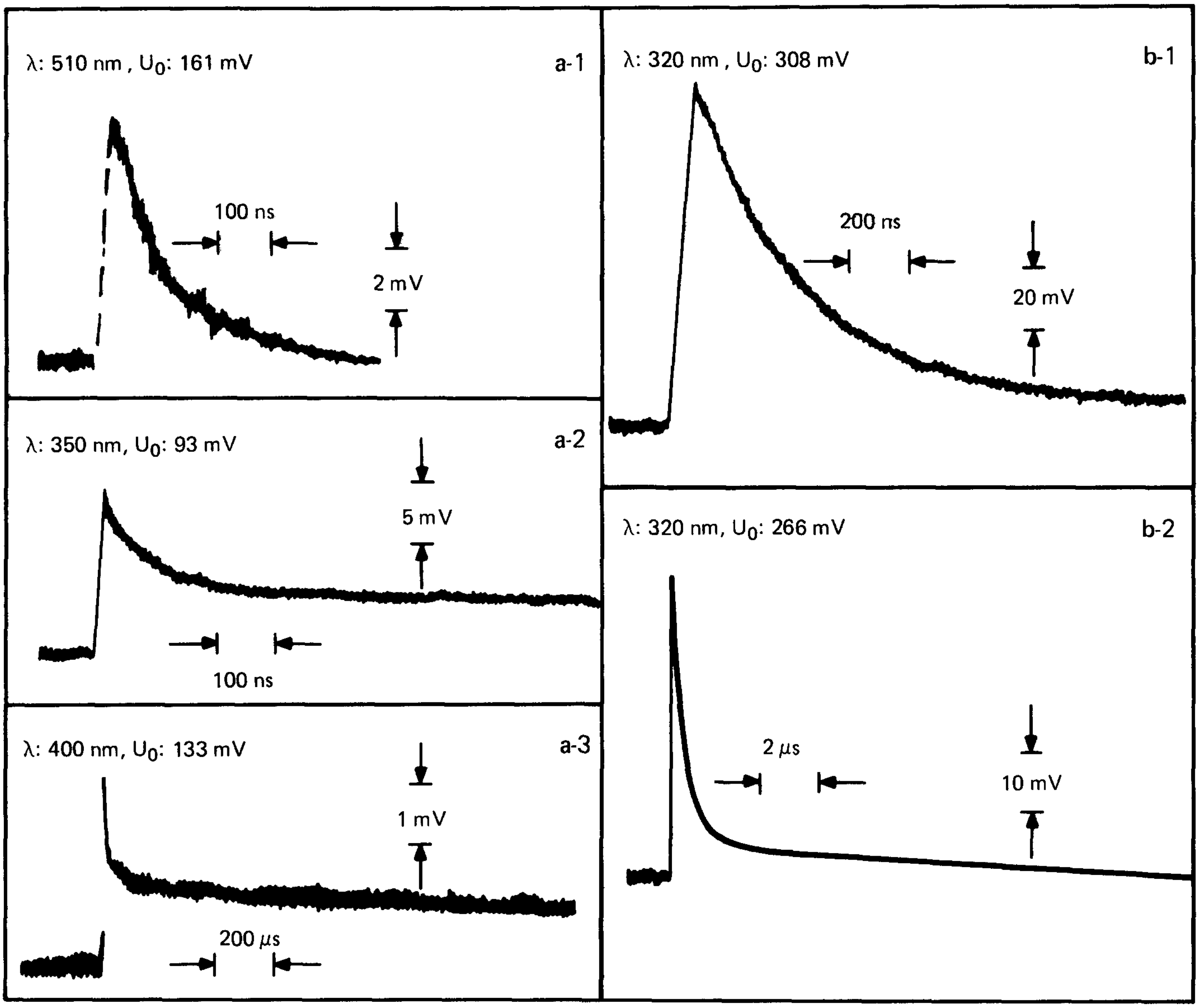


Figure 2 Typical oscilloscope traces obtained with benzene solutions of (a) PPIK (1.5×10^{-3} base mol/l) and (b) pivalophenone (2.6×10^{-3} mol/l). Absorbed dose per flash in einstein/l: 1.4×10^{-5} (a-1 to a-3); 6.2×10^{-6} (b-1); 4.8×10^{-6} (b-2)

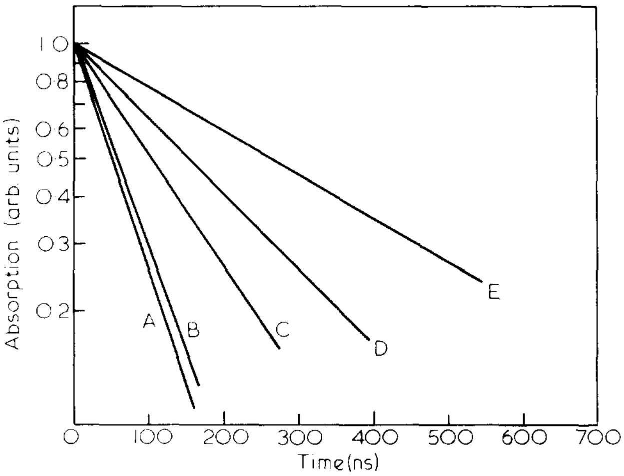


Figure 3 First order plots demonstrating the decrease of the transient absorption at λ = 460 nm [PPIK (A) and CP-St-PIK-12 (B)] and at 320 nm [CP-St-PIK-3.7 (C), CP-St-PIK-1 (D) and pivalophenone (E)]. Solute concentrations are given in the last column of *Table 1*. Solvent: benzene. Absorbed dose per flash: 1.4×10^{-5} einstein/l

immediately after the flash was observed. However, the lifetime of the short-lived absorption was significantly reduced indicating a reaction of the triplets with 2-propanol. Pseudo-first order kinetic treatment of the data yielded $k(T + \text{2-propanol}) = (2.0 \pm 0.2)\ 10^6$ l/mol sec.

In *Figure 4* spectra are compared which were obtained with benzene and benzene–2-propanol (1:1 vol/vol) solutions of PPIK 150 μsec after the flash. The difference spectrum is attributed to the ketyl radical for its resembling strongly the ketyl radical spectrum observed with acetophenone[7]. Thus it becomes evident that the spectrum formed in the presence of 2-propanol is composed of the absorptions of both the ketyl radical generated by the reaction of 2-propanol with excited ketone groups and by the benzoyl-radical formed during α-cleavage.

Copolymers

Flash photolysis experiments carried out with random copolymers of PIK and St containing 1 to 12 mol % PIK yielded the same initial transient spectrum as the one ob-

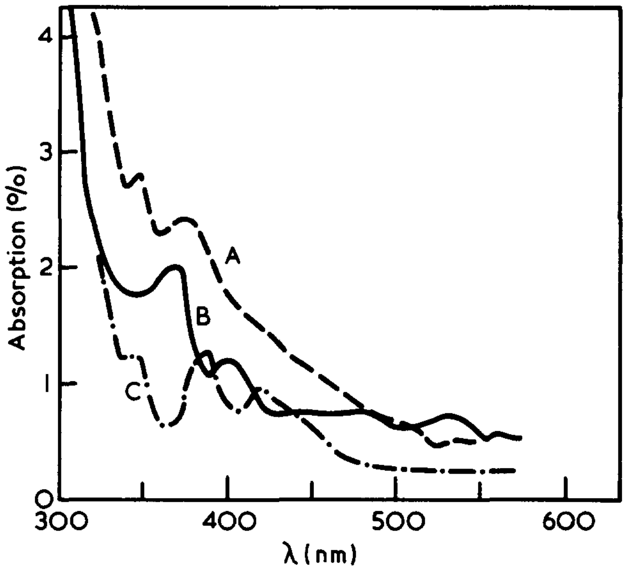


Figure 4 Transient spectra recorded 150 μsec after the flash. Solutions of PPIK in (a) benzene-2-propanol (1:1, Vol/Vol) and (b) benzene. [PPIK] : 1.5 x 10^{-3} base mol/l. Absorbed dose per flash: 1 x 10^{-5} einstein/l (c): difference spectrum

tained with homo PPIK. Furthermore, the same initial spectrum was observed in benzene, benzene/2-propanol (1:1 vol/vol) and tetrahydrofuran solutions. In all cases two modes of decay of the transient spectra were observed. In the wavelength range between 330 and 370 nm only the short-lived decay was detected. First order plots demonstrating the decay of the absorption are shown in *Figure 3*. Furthermore, in this wavelength range a strong emission was seen which exhibited a maximum at 360 nm and decayed during the flash. At the other wavelengths a long-living absorption remained (see *Figure 5*).

By quenching experiments with naphthalene and biphenyl the short-lived absorption was identified as the *T–T* absorption of excited PIK moieties in analogy to the experiments with the homo PPIK.

The lifetime of the short-lived mode increased with decreasing intensity of the incident light. Rate constants obtained by extrapolation to zero intensity are: (8 ± 1) x 10^6 sec^{-1} (CP–St–PIK–12), (6 ± 1) 10^6sec^{-1} (CP–St–PIK–3.7) and (3 ± 1) 10^6sec^{-1} (CP–St–PIK–1). From these results it is inferred that different decay mechanisms become operative at different polymer composition. This is also demonstrated by *Figure 5*, where the spectra of the long-lived species obtained upon the irradiation of homo-PPIK and of CP–St–PIK–1 are compared. One sees that the decay of the initially absorbing species obviously leads to different products. In the case of homo-PPIK the spectrum is essentially due to that of benzoyl radicals, whereas in the case of poly(styrene-co-isopropenyl ketone) the long lived spectra are composed of spectra of the various radicals formed by α-cleavage and type II processes. The tendency for α-cleavage decreases as the PIK content in the copolymers decreases. In the case of CP–St–PIK–1 the spectrum is almost completely identical with that of the ketyl radical in this wavelength range (see *Figure 5*). O_2 accelerated the decay of the short-lived species (k_{O_2} = (3 ± 2) 10^8 l/mol sec) Generally, the long-lived species was formed simultaneously with the decay of the short-lived absorption. In oxygen-saturated solution the formation of the long-lived species was strongly inhibited.

Pivalophenone

Transient spectra obtained upon irradiating pivalophenone in benzene solution are shown in *Figure 1b*. Two modes of decay of the absorption were observed in the wavelength range investigated. *Figure 2b* presents typical oscillograms. It is seen from *Figure 1b* that after the decay of the short-lived absorption a rather long-lived spectrum remains which is assigned to the benzoyl radical. The short-lived major portion of the absorption decays according to a first-order process. The rate constant k_T = (2.7 ± 0.2) 10^6 sec^{-1} was found to be independent of the incident light intensity. It is about 4 times lower than the respective rate constant in the case of PPIK.

In the presence of naphthalene and biphenyl the formation of *T–T* absorption of the quenchers was observed. Typical oscilloscope traces obtained with naphthalene containing solutions are shown in *Figure 6*. The *T–T* absorption of the quenchers increased with increasing quencher concentration. A Stern–Volmer analysis of these data yielded in both cases k_q = (2.0 ± 0.4) 10^9 l/mol sec. Based on these k_q values one obtains from the results of Lewis and Magyar[3] a k_T value which is of similar magnitude as the one found in this work. Those authors evaluated k_T by assuming k_q = 5 x 10^9 l/mol sec.

Experiments carried out with solutions of pivalophenone in 2-propanol yielded the following results: the spectrum observed immediately at the end of the 25 nsec flash was almost identical to the respective spectrum obtained in benzene solution (see *Figure 1b*). The peak at low wavelength, however, was red-shifted (from 335 nm in benzene to 360 nm in 2-propanol). Surprisingly, the spectrum, which is assigned to the triplet state, was decaying more slowly than in benzene [at constant intensity of incident light the first order lifetimes are τ = 374 nsec (benzene) and τ = 500 nsec (2-propanol)]. It furthermore appeared that α-cleavage is strongly suppressed in 2-propanol as is inferred from the spectrum observed 150 μsec after the flash. This spectrum

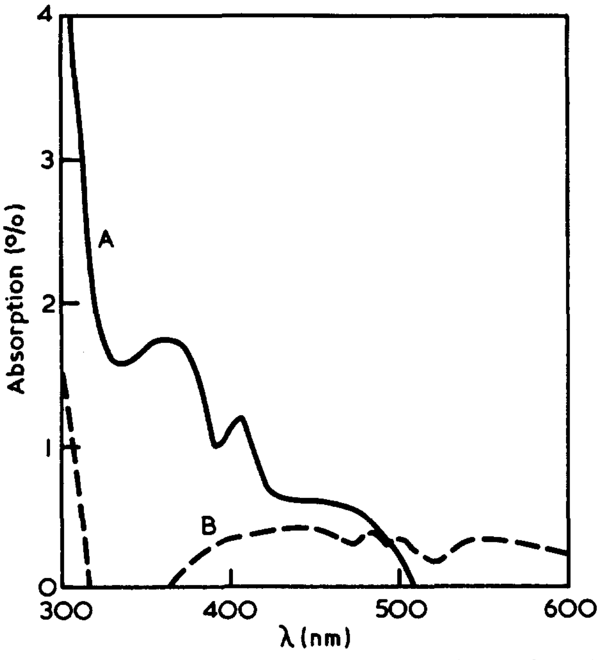


Figure 5 Transient spectra recorded 150 μsec after the flash obtained with benzene solutions of (A) PPIK (1.5 x 10^{-3} base mol/l) and (B) CP-St-PIK-1 (1.5 x 10^{-1} base mol/l) at room temperature. Absorbed dose per flash: 1 x 10^{-5} einstein/l

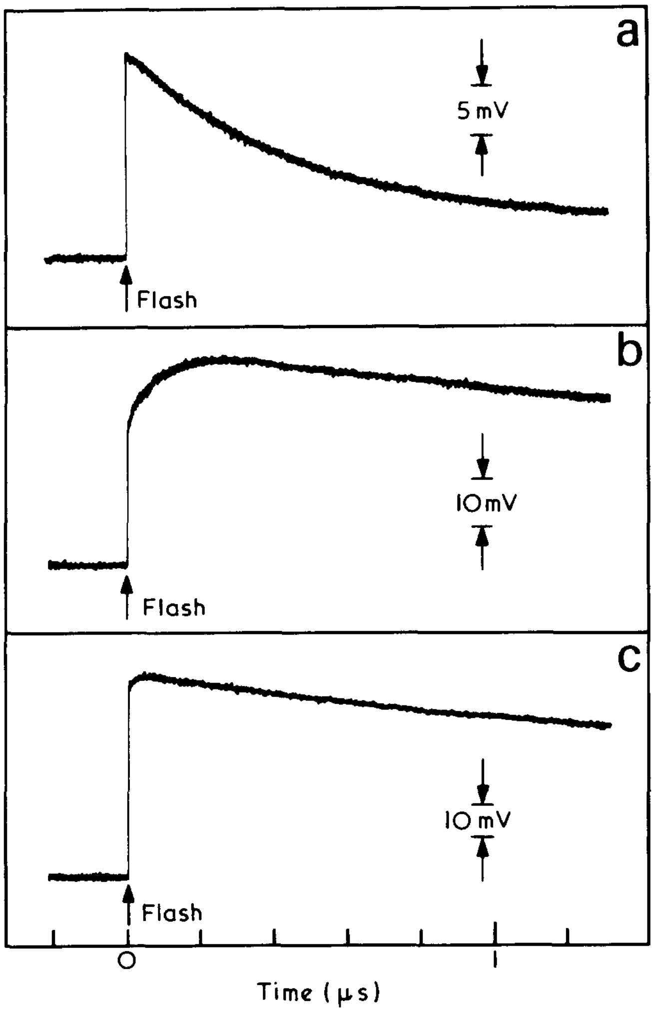
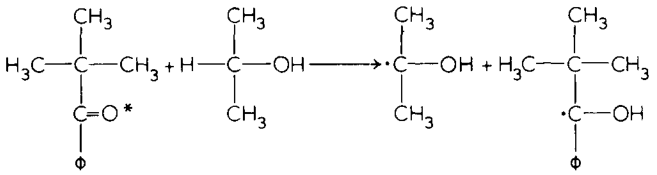


Figure 6 Oscilloscope traces obtained with benzene solutions of pivalophenone (2.6 x 10^{-3} mol/l) demonstrating the change of the optical absorption at 413 nm after a 25 nsec flash (absorbed dose per flash: 1.4 x 10^{-5} einstein/l). (a) No naphthalene present, U_0 = 182 mV; (b) [Naph] : 2.0 x 10^{-3} mol/l, U_0 = 186 mV; (c) [Naph] : 2.0 x 10^{-2} mol/l, U_0 = 180 mV

indicated the existence of ketyl radicals which are presumably generated by the reaction



$$H_3C-C(CH_3)_2-C(=O^*)\Phi + H-C(CH_3)_2-OH \longrightarrow \cdot C(CH_3)_2-OH + H_3C-C(CH_3)_2-\cdot C(OH)\Phi$$

The ketyl radical spectrum decayed with a first half-life time of about 10 msec.

DISCUSSION

The results show that the triplet state of excited carbonyl groups is relatively long-lived in the polymers investigated (k_T: 5 to 10 x 10^6 $\sec^{-1}$). In the case of pivalophenone which is considered a model compound for PPIK, k_T is significantly smaller (2.5 x 10^6 $\sec^{-1}$). If $T-T$ deactivation processes can be neglected (by considering only k_T values obtained by extrapolation to zero incident intensity) the triplet decay rate constant k_T can be expressed as:

$$k_T = k_I + k_{II} + k_d + k_{RH}[RH] + k_q[Q] \qquad (1)$$

For the quantum yields of special deactivation route expressions such as the one for α-cleavage can be derived:

$$\phi(I) = \phi(T)\frac{k_I}{k_I + k_{II} + k_d' + k_{RH}[RH] + k_q[Q]} \qquad (2)$$

where k_I: 1st order rate constant for the Norrish type I reaction (α-cleavage); k_{II}: 1st order rate constant for the Norrish type II reaction (main chain rupture); k_d' : 1st order rate constant for all non-chemical deactivation processes (Σk_d); k_{RH}: 2nd order rate constant of the reaction T + RH, T, denoting triplet and RH a hydrogen donor (including the polymer or model compound); k_q: 2nd order rate constant of the reaction of triplets with a quencher Q added to the system.

The quantum yield for triplet formation was determined from the limiting optical densities of the $T-T$ absorption of naphthalene obtained by the extrapolation of [Naph] $\rightarrow \infty$ (from plots of OD^{-1} vs. $[\text{Naph}]^{-1}$). The respective limiting OD value for acetophenone was also determined and was used as a reference value: $\phi(T)$ = 1.0 has been reported[11] by other authors. Thus, for homoPPIK,$\phi(T)$ = 0.70 ± 0.05, for the copolymers of St and PIK,$\phi(T)$ = 0.6 ± 0.1 and for pivalophenone,$\phi(T)$ = 0.80 ± 0.05 were determined.

In the cases of homo-PPIK and pivalophenone k_{II} can be neglected. However, for lack of knowledge of k_d' and k_{RH} a final conclusion cannot yet be drawn concerning the question why $k_T(\text{PPIK}) \approx 4k_T(\text{pivalophenone})$.

It is interesting to note that k_T is decreasing with decreasing content of PIK in the St-PIK copolymers. However, as is inferred from the spectra obtained at relatively long times after the flash and from the finding that main chain scission is occurring, α-cleavage is obviously not the predominant route of chemical triplet deactivation during the irradiation of the copolymers. Type II processes and inter- and/or intramolecular hydrogen abstraction reactions are becoming important. This shows that k_I is clearly strongly dependent on the chemical nature of moieties in neighbouring positions to base units containing excited carbonyl groups. Due to strong next neighbour influences k_I might actually be greater for PPIK than for pivalophenone and the difference of k_T values might be caused essentially by the difference of k_I values.

Another interesting feature detected during this work concerns the finding that PPIK carbonyl triplets are interacting faster with 2-propanol than pivalophenone triplets. This effect is probably at least to some extent due to the fact that in benzene/2-propanol mixtures PPIK molecules are preferentially solvated by benzene molecules. The latter permit the occasional attack of excited carbonyl groups by alcohol molecules. On the other hand, alcohol molecules interact with ground state pivalophenone molecules rather strongly.

Thus, the decreased excited state reactivity observed in this case might be explained in a similar way as substituent effects on the efficiency of phenyl ketone hydrogen abstraction. In that case the decreased reactivity results from lowered energy levels of the unreactive[3] (π,π^*) state relative to that of the reactive $^3(n,\pi^*)$ state.

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