Photophysics and photochemistry of poly (4′-ethoxyacrylophenone)

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Abstract

The photophysics and the long wave ($\lambda \geq 300$ nm) photochemistry of poly (4′-ethoxyacrylophenone) were investigated. The quantum yield for fluorescence is low (10^{-4} mol (einstein)$^{-1}$), and the principal excited species is the carbonyl triplet. The quantum yield for phosphorescence is greater and the λ_{max} value is 445 nm. The triplet lifetime at 77 K is 0.41 s, but 8.7 μs at 300 K. These observations are consistent with the formation of a low-lying triplet, which, in turn is the result of substitution of the aromatic ring with the electron donating ethoxy group. The principal photoprocess occurring in dilute solution (in CH_2Cl_2) of the polymer is a Norrish Type II decomposition, which results in random chain scission and a rapid decrease in the molecular weight. The relatively low quantum yield (6×10^{-2} mol (einstein)$^{-1}$) for the scission process reflects the low reactivity of a triplet (which has some π, π^* character) in abstraction reactions. In the case of PEAP, H-abstraction is a prerequisite for biradical formation, which, in turn leads to chain scission. Chain scission was subject to inhibition by triplet quenchers, such as naphthalene and *cis*-1,3-pentadiene, and the data conformed to Stern–Volmer kinetics. However, the quenching rate constants, k_Q were lower in magnitude than the corresponding diffusion controlled values, and it is proposed that this is principally due to a steric effect, the actual encounter of the quencher with the carbonyl triplet being subject to adverse steric interactions associated with the proximity of the relatively bulky polymer chain. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Photophysics; Photochemistry; Poly(5′-ethoxyacrylophenone); Triplets; Quantum yields; Quenching; Chain scission

1. Introduction

The photophysics and photochemistry of poly (acrylophenone) and its methoxy analogues have been the subject of a number of studies, extending over two decades [1]. Earlier investigations showed that the principal photo-process which occurred when the polymers were irradiated with long-wave UV light in dilute solution was Norris Type II reaction, which, in turn lead to random chain scission [2–4]. It was also established that the principal excited species was the carbonyl triplet, which was formed in high quantum yield and rapidly from the initially formed singlet n→π* state [1]. Qualitatively similar results were obtained when the polymers were irradiated in the solid state. However, the quantum yields for chain scission were considerably lower, self-quenching by the terminally unsaturated ketonic entities (formed in the Norrish II reaction) being more probable in the solid state. In addition, the higher viscosity of the solid state restricts conformation mobility, and this results in a lower rate of collapse of the biradical — a prerequisite for chain scission [5]. Later, more detailed photophysical investigations showed that the n→π* triplet in the methoxylated polymer (i.e. poly (3′,4′-dimethoxyacrylophenone) and poly (3′,5′-dimethoxyacrylophenone) had appreciable n→π* character, and were consequently less reactive in abstraction reactions, and this was reflected in the values of the quantum yields for chain scission [6,7].

So far, no study of the homologous poly (4′-ethoxyacrylophenone) (PEAP) has been made, and the work described below was undertaken as part of a general study of the effect of ring substitution on the photophysical properties and the photochemistry of the poly (acrylophenones).

2. Experimental

2.1. Materials

The monomer, 4′-ethoxyacrylophenone, was prepared by the Friedel–Crafts acetylation of ethoxybenzene, followed by dehydrochlorination with ethanol and potassium acetate. Reaction conditions were similar to those previously employed [8]. Polymerization was carried out in bulk at 343 K, under high vacuum and in the absence of initiator, and the reaction was quenched (liquid N_2) after about 10% conversion. The polymerization proceeds rapidly at lower temperatures, but they cannot be used, since the resulting

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very high molecular weight polymers form gels, which are impossible to characterize. The polymer was recovered by precipitation of the reaction mixture in pure MeOH, and it was purified by repeated dissolution in CH_2Cl_2 followed by precipitation in the MeOH. After drying under vacuum at 343 K, the polymer was stored in the dark.

2.2. Analytical techniques

UV–VIS spectra were obtained using a Lambda II spectrophotometer (Perkin Elmer) and emission spectra were recorded using LS5OB luminescence spectrometer (Perkin Elmer), which was also used to measure phosphorescence lifetimes at 77 K.

2.3. Photochemical techniques

Polymers were exposed to UV ($\lambda \geq 300$ nm) radiation under vacuum (10^{-5} kPa) in CH_2Cl_2 solutions (7×10^{-2} M). Before irradiation, the solutions were thoroughly outgassed under vacuum. The Pyrex reaction vessel was thermostated to 298 ± 0.1 K, the UV source was a medium pressure Hg arc (Hanovia 200 W). Details of the system have been published elsewhere [9]. Quantum yields for chain scission were estimated by photochromic actinometry, the extent of absorption in the photo-active region of the UV being determined by UV spectrometry [10].

2.4. Transient measurements

Polymer solutions (in CH_2Cl_2) were degassed and irradiated at 300 K with pulses of 8–10 ns duration (10 mJ per pulse at 337.1 nm) from a nitrogen laser (Molectron UV-24). A detailed description of the equipment and technique has been published [11].

2.5. Molecular weights

Number average ($\bar{M}_n$) molecular weights of the original polymer and those of polymers undergoing degradation were determined by gel permeation chromatography, using Waters equipment in conjunction with a UV detector and Ultrastyragel columns. The system was calibrated with narrow range poly(styrene) standards. The progress of chain scission was also monitored by GPC, the number average molecular weight being measured as a function of radiation dose. The unreacted polymer had an ($\bar{M}_n$) value of 10^5.

3. Results

Fig. 1 shows the UV spectrum of a dilute solution (10^{-3} M) of PEAP. (The absorption characteristics of a film are very similar). The intense short-wave absorption ($\lambda_{max} = 280$ nm) is due to the symmetry forbidden $\pi \rightarrow \pi^*$

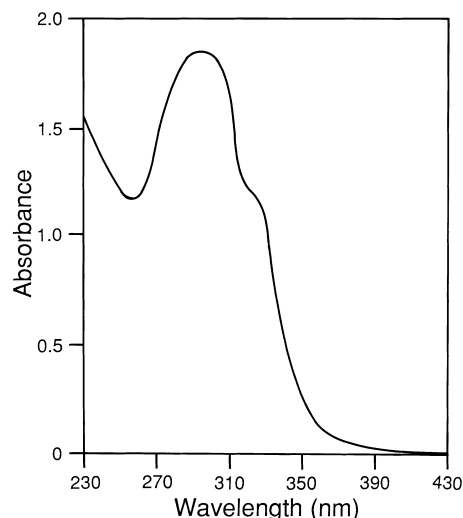Fig. 1. UV absorption spectrum of PEAP in CH_2Cl_2 (concentration $=10^{-3}$ M).

transition of the phenyl group. The longer wave absorption, ($\lambda_{max} = 325$ nm approximately) due to the $\pi \rightarrow \pi^*$ transition of the carbonyl, is not well resolved, overlapping to a large extent with the $\pi \rightarrow \pi^*$ band. The emission characteristics of PEAP are shown in Fig. 2 (fluorescence) and 3 (phosphorescence) along with the corresponding excitation spectra. The fluorescence spectrum, measured in CH_2Cl_2 solution at 300 K exhibits a typical mirror image relation to the excitation spectrum, and the relatively small Stokes shift implies that the geometries of the ground and the S_1 states are similar. The quantum yield, $\Phi_F = 10^{-4}$ mol (einstein)$^{-1}$. The instrument was calibrated with dibenzyl ketone [12]. As in the case of other aromatic ketones, low flourescence quantum yields reflect the high probability of ISC [13]. Both intensity and quantum yield (Φ_p) of phosphorescence are much greater ($\Phi_p = 7 \times 10^{-2}$ mol (einstein)$^{-1}$), and the triplet energy, $E_T(0-0)$ is $267 \pm 5\%$ kJ mol^{-1}. The decay
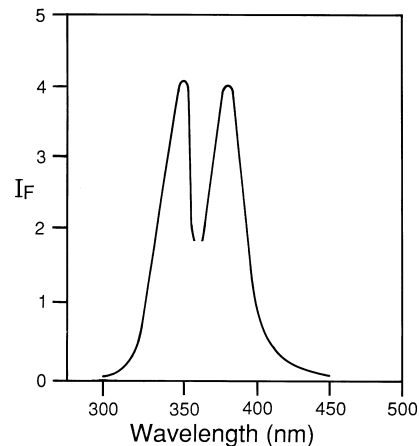

Fig. 2. Fluorescence spectrum of PEAP (CH_2Cl_2 solution$=5 \times 10^{-3}$ M at 300 K). Fluorescence intensity, I_P is in arbitrary units.
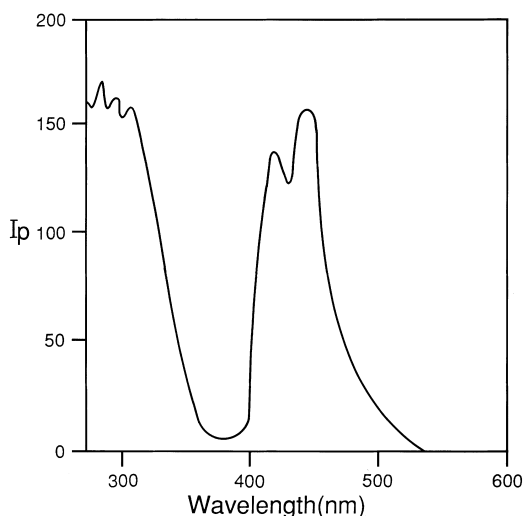
Fig. 3. Phosphorescence spectrum of PEAP in glass at 77 K. Phosphorescence intensity, I_P is in arbitrary units.

Fig. 5. Decay of the PEAP triplet in degassed CH_2Cl_2 solution at 300 K, monitored at 390 nm.

characteristics of the triplet were investigated at 77 K, and a single exponential was obtained. The data are summarized in Fig. 4 (linear and semi-log plots) and a lifetime of the triplet at 77 K of 0.41 s can be inferred.

Laser excitation of degassed solutions of PEAP produced a new transient absorption in the 385–405 nm region, and this was attributed to the carbonyl triplet. The time decay characteristics are shown in Fig. 5, the change in optical density being monitored at 390 nm. From the data, a triplet lifetime, τ_T, of 8.7 µs at 300 K can be derived. The five orders of magnitude difference in the lifetime at 300 K (relative to that 77 K) is typical of acrylophenone polymers [1,6].

By far, the most important manifestation of photochemical reactivity was the rapid reduction of the molecular weight of PEAP. Typical data for a CH_2Cl_2 solution are shown in Fig. 6 in which the molecular weight changes are represented by S, the number of chain scissions per original macromolecule.
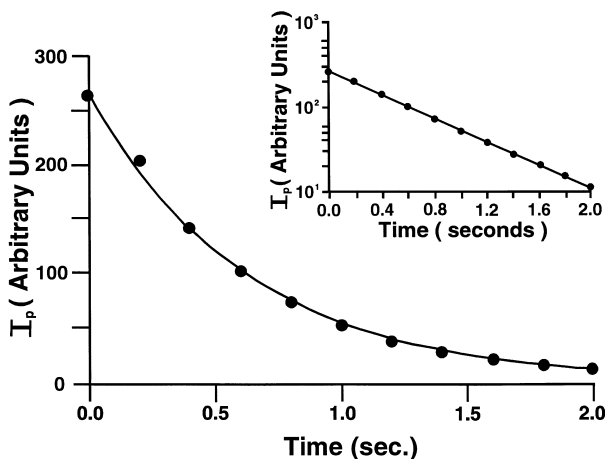
The linearity, which is evident particularly in the earlier stages of the reaction, implies that random chain scission is occurring. (The lack of linearity in the subsequent stages of the reaction will be discussed below). The quantum yield for chain scission, Φ_{cs} is given by the expression

$$\Phi_{cs} = \frac{\text{Number of moles, } n, \text{ of chain scission in time } t}{I_A t} \quad (1)$$

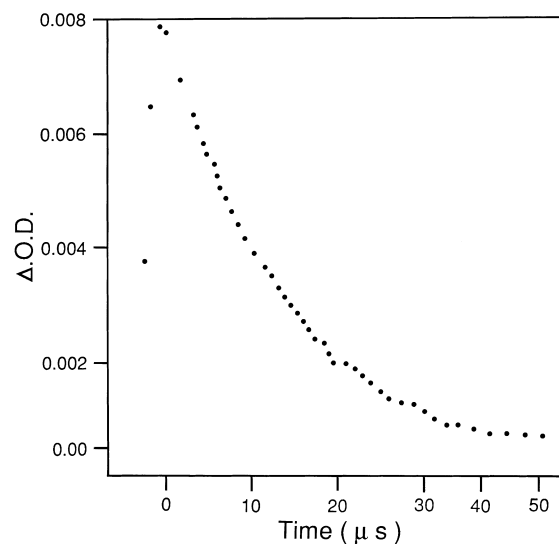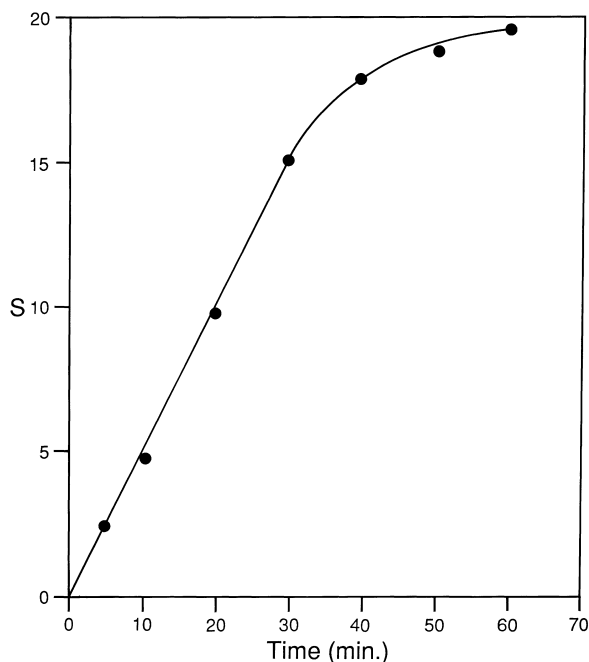Fig. 4. Decay characteristics of the PBAP triplet at 77 K, shown as I_P vs. time. Inset: the semi-logarithmic plot.

Fig. 6. Molecular weight decreases as a function of time of irradiation of PEAP in CH_2Cl_2 solution (5×10^{-3} M) at 300 K ($\lambda \geq 300$ nm and $P = 10^{-5}$ kPa). Data shown are S, the number of chain scissions per original macromolecule, as a function of time.

in which I_A is the number of Einsteins of photons absorbed in unit time. I_A is related to the incident intensity, I_0, as

$$I_A = I_0[1 - \exp(-\varepsilon Cl)] \tag{2}$$

where ε is the absorption coefficient, C is the concentration and l is the effective path length of the solution. The number of moles, n is related to the observed molecular weight changes by (3) [14], i.e.

$$n = \frac{w}{(\bar{M}_n)_0} \left\{ \frac{(\bar{M}_n)_0}{(\bar{M}_n)_t} - 1 \right\} \tag{3}$$

in which $(\bar{M}_n)_0$ and $(\bar{M}_n)_t$ are, respectively, the original number average molecular weight, and that after time t of irradiation, and w the mass of polymer undergoing photolysis. Substitution in (1) yields

$$\Phi_{cs} = \frac{w[(\bar{M}_n)_0/(\bar{M}_n)_t - 1]}{(\bar{M}_n)_0 I_0[1 - \exp(-\varepsilon Cl)t]} \tag{4}$$

I_A was determined from UV absorption data, and actinometry and a value of 6×10^{-2} mol (einstein)$^{-1}$ was obtained for Φ_{cs}. The effects of triplet quenchers were investigated. Addition of naphthalene to the films reduced the phosphorescence intensity at 77 K (Fig. 7). It is clear that, despite the limited mobility in the solid state at 77 K, naphthalene is effectively quenching the PEAP triplet. Similarly, the effects of naphthalene and *cis*-1,3-pentadiene on the rates of chain scission are shown in Fig. 8, in which quantum yield ration (Φ_0/Φ) for chain scission in presence of (Φ) and in absence of quencher Q (Φ_0) are shown as a function of the quencher concentration, [Q]. It can be seen that data for both quenchers (Fig. 8) conform satisfactorily to Stern–Volmer kinetics, i.e.

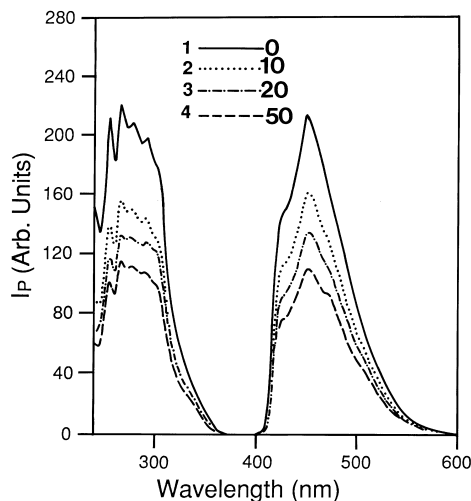$$\frac{\Phi_0}{\Phi} = 1 + K_{sv}[Q] \tag{5}$$

Fig. 7. Effects of naphthalene on the phosphorescence characteristics of the PEAP film at 77 K. Numbers (0–50) represent the concentrations of naphthalene (w/w%).
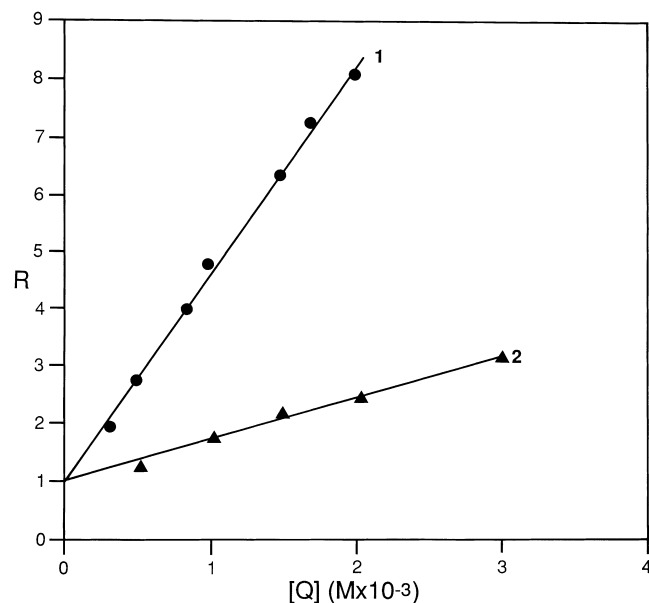

Fig. 8. Quantum yield ratio, $R(=\Phi_0/\Phi)$ as a function of quencher concentration, [Q] 1: +naphthalene, 2: + *cis*-1,3-pentadiene.

in which K_{sv} is the Stern–Volmer constant, which is in turn, related to both triplet lifetime, τ_T and the quenching rate constant, k_Q Values (i.e. values of 6×10^8 dm^3 mol^{-1} s^{-1} and 1.9×10^8 dm^3 mol^{-1} s^{-1} for naphthalene and *cis*-1,3-pentadiene respectively, were obtained. These data also confirm the involvement of the triplet in the chain scission process.

Photophysical and photochemical parameters for PEAP are compared with those of the closely related poly (4'-methoxyacrylophenone) (PMAP) in Table 1. With the exception of the values for λ_{max} and quantum yield for fluorescence and the triplet lifetimes at 77 K, which were re-determined in this study, data for PMAP and PDMAP were taken from the literature [1,6]. All of the data for PEAP are subject to an uncertainty of ±5%.

4. Discussion

UV spectra of methoxylated aromatics are rarely well resolved, and that of PEAP is no exception (Fig. 1). Substitution of electron-donating groups (like MeO) in the benzene ring perturbs the energies of the bonding and anti-bonding π-electrons, and this produces a bathochromic shift in the symmetry forbidden π→π* transitions (i.e. $^1A_{1g} \rightarrow {}^1B_{1u}$ and $^1A_{1g} \rightarrow {}^1B_{2g}$) There are two important consequences of this. In the first place, the lower intensity $^1A_{1g} \rightarrow {}^1B_{2u}$ band becomes buried in the more intense $^1A_{1g} \rightarrow {}^1B_{1u}$, band, and this, in turn overlaps the n→π* band due to the carbonyl, to the extent that the carbonyl absorption appears as a shoulder only. The increased substitution in the ring also leads to a reduction in the D_{6h} symmetry, and with it a relaxation of the forbidden character of the π→π* transitions and this is reflected in the

Table 1
Comparison of photophysical and photochemical data for poly(acrylophenones)

Polymer	Fluorescence λ_{max} (nm)	Phosphorescence λ_{max} (nm)	Φ_F at 300 K mol (einstein)$^{-1}$	τ_T at 77 K (s)	τ_T at 300 K (μs)	k_Q[a] at 300 K (dm^3 mol^{-1} s^{-1})	Φ_{cs} at 300 K mol (einstein)$^{-1}$
PMAP	362	430	1.5×10^{-4}	0.31	4.6	7.6×10^8	10^{-1}
PDMAP	390	490	2.4×10^{-5}	0.55	28.3	1.6×10^8	1.6×10^{-4}
PEAP	380	445	10^{-4}	0.41	8.7	6.0×10^8	6×10^{-2}

[a] With naphthalene.

higher intensity of the combined band (c.f. unsubstituted analogues). Secondly, the long wave chromophore becomes a composite one, and the excitation of the carbonyl can be delocalized over the aromatic π-system [15].

A similar bathochromic shift is observed in the phosphorescence spectrum (Fig. 7), and the vibrational structure is typically absent from the emission spectrum.

The effect of methoxy substitution on the character of the n→π^* triplet is also marked. Because of the energetic proximity of the n, n* and the π, π^* (aromatic triplets, configurational mixing and vibrational coupling can occur, and as a result, the n, π^* triplet acquires some π, π^* character). Methoxy ketones have typically low-lying π, π^* and this is reflected in their lower reactivities and their extended lifetimes [16] (Table 1).

Decreases in molecular weight can be attributed to random chain scission, which, in turn can be attributed to a Norrish type II decomposition, which is mediated by a γ-H-abstraction by the carbonyl triplet. The magnitude of the quantum yield for chain scission (Table 1) is typically low and is a further manifestation of the low reactivity of the triplet towards abstraction, and this, in turn is the behaviour of triplets having π, π^* [6,17].

The lack of linearity of the data in Fig. 6 suggests that after comparatively small doses, the chain scission is susceptible to inhibition. (At these low extents of reaction, there is no question of substrate depletion). An obvious source of inhibition is the quenching of the carbonyl triplet by the unsaturated ketonic moieties that are formed at the chain ends during the Type II photodecomposition [5]. Such species appear to be particularly effective quenchers, the increased activity being associated with their chain end location, which allows them to act as traps for any migrating triplet energy [1].

The linearity of the semi-log plot (Fig. 4) and the shape of the decay curve (Fig. 5) indicate that only one excited species (i.e. the triplet) is involved, and this can be reconciled with the low fluorescence intensity (Fig. 2) and the very small quantum yield for fluorescence (Table 1). The results of quenching studies (with efficient triplet quenchers confirm this proposition).

While the quenching data (based upon the inhibition of chain scission) conform well to Stern–Volmer kinetics (Fig. 8), the magnitudes of the quenching constants, k_Q, derived from K_{sv} values are smaller than those expected for a diffusion-controlled process. For example, k_Q for naphthalene is 6×10^8 M^{-1} s^{-1} at 300 K, compared to typ-

ical diffusion controlled values in the 5×10^9–10^{10} M^{-1} s^{-1} range at 300 K. It is unlikely that this discrepancy can be attributed to adverse enthalpic factors, since the triplet energy level in PEAP lies at least 12 kJ mol^{-1} above that in naphthalene.

Restricted mobility of the chromophore due to the limited diffusion of the polymer has been invoked to account for the different k_Q values, [18] and in the present case, the high degree of polymerization will lead to increased entanglement, and hence lower mobility. However, from a quantitative point of view, these factors are insufficient to account for the large differences, since complete immobilization of the chromophore would reduce the k_Q value by a factor of two only.

The actual encounter process must also be considered. Energy transfer from excited triplets occurs by the exchange mechanism, [17] which requires close approach of donor and acceptor orbitals. The specific relative orientations of the CO group and the quencher, required for optimal energy transfer may not necessarily be achieved, if the presence of the adjacent polymer chain restricts access to the CO group; i.e. the collision is less effective, and the rate constant will be less than the diffusion controlled value, which, in turn assumes that energy transfer occurs on each collision.

Stereo-electronic restrictions of orbital interaction, which have previously been invoked to account for limited efficiencies of energy transfer [19] are independent of the diffusion processes, but can nevertheless, contribute to the reduction in k_Q value. A similar conclusion has been reached by Scaiano [6].

The efficiency of quenching can also be reduced by triplet energy migration along the chain, and similarly the new terminal vinyl ketone groups, formed in the Type II reaction, can act as efficient quenchers [20]. These processes would effectively reduce the triplet lifetime, and thus the experimental value of K_{sv} from which k_Q is derived, will be smaller. It is not, however, possible to assess the contributions of each of these various factors in a quantitative sense.

Acknowledgements

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