The triplet lifetime of poly(phenyl vinyl ketone). A laser flash photolysis study*

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The photochemistry of poly(phenyl vinyl ketone) in solution has been examined over a temperature range using nanosecond laser flash photolysis techniques. Experiments were performed at low temperatures to eliminate the interference from biradical signals and allow for the separation in time of the behaviour of quencher-free and quencher-containing polymers. For the former the kinetics of triplet decay in toluene-d_8 lead to log $(A/s^{-1}) = 9.90 \pm 0.50$ and $E_a = (3.56 \pm 0.30)$ kcal mol^{-1} where A is the preexponential factor and E_a the activation energy. The extrapolated triplet lifetime at 20°C is 57 ns.

Keywords Photolysis; triplet lifetime; poly(phenyl vinyl ketone); laser flash photolysis; quencher-free polymers; quencher-containing polymers

INTRODUCTION

The photochemistry of poly(phenyl vinyl ketone), PPVK, has been the subject of numerous investigations that have included quantum yield and kinetic studies[1-11]. Despite these, the lifetime of the triplet state of PPVK (τ_t) is still a matter of speculation. Competitive studies, based on photodegradation experiments, are faced with the shortening of the triplet lifetime as a result of the degradation which is known to incorporate quencher end-groups in the macromolecule[6]. Direct laser flash photolysis studies are complicated by the extensive overlap, in both wavelength and time, of the signals due to the biradical and the triplet state[4,8]. Stern–Volmer studies using laser techniques (e.g. using naphthalene as a triplet energy acceptor) lead to good values of the product $k_q\tau_t$, but the absolute value of τ_t is ultimately based on the assumption of a value for the quenching rate constant, k_q[9]. Furthermore, quenching techniques usually assume that the starting polymer does not contain any quencher groups; since these can be incorporated during the preparation, purification and handling of the polymer or its solutions, the validity of the assumption is difficult to evaluate.

We have recently observed that the lifetimes of triplet biradicals are temperature independent or nearly so[12-14], while the Norrish Type II reaction which controls the triplet lifetimes is an activated process[15]. Thus, at low temperatures one can expect the triplet lifetime to be long in comparison with the biradical lifetime; under these conditions the direct measurement of τ_t using flash techniques should be possible. One can also take advantage of spectroscopic differences: e.g., at 365 nm the extinction coefficient of the triplet is considerably larger than that for the biradical. The combination of these effects minimizes the interference due to biradical absorptions.

In a recent study[16] on the photochemistry of poly(p-methoxyacrylophenone) we have shown that the photobehaviour of quencher-containing and quencher-free macromolecules results in fast and slow components in the triplet decay and that these can be easily separated. These ideas can also be applied to the case of PPVK, where low temperature studies should facilitate the study of the photobehaviour of quencher-free and quencher-containing macromolecules.

EXPERIMENTAL

The sample of PPVK used for these studies was obtained by free radical polymerization of a deoxygenated solution of phenyl vinyl ketone (25%, 50°C) in benzene containing 1% tert-butyl hyponitrite as initiator. All procedures for preparation and purification are the same as reported earlier[6] and conversions were kept below 20%. The molecular weight of the sample was 35 000[2].

The solvents used were of the highest purity commercially available and were used as received. Toluene-d_8 was preferred over toluene in an attempt to minimize the possibilities of ketone photoreduction.

Laser excitation was carried out using the pulses (337.1 nm, ~8 ns, up to 10 mJ) from a Molectron UV-24 nitrogen laser for excitation. Our system allows measurements of transient absorptions in the 10 ns to 100 μs time range and has been interfaced with a PDP11/03L computer that controls the experiments and provides suitable data gathering, processing, storage and hardcopy facilities. Further details have been given elsewhere[17].

RESULTS AND DISCUSSION

Triplet lifetimes for poly(phenyl vinyl ketone) were monitored at 365 nm over as wide a temperature range as possible in toluene-d_8 and chloroform. Our earlier studies[9] led to a biradical lifetime (see Scheme I) of 65 ns (benzene); we have therefore regarded as reasonably accurate triplet lifetime values exceeding ~150 ns, this being the condition determining the upper temperature limit in our studies. *Table 1* summarizes the results from

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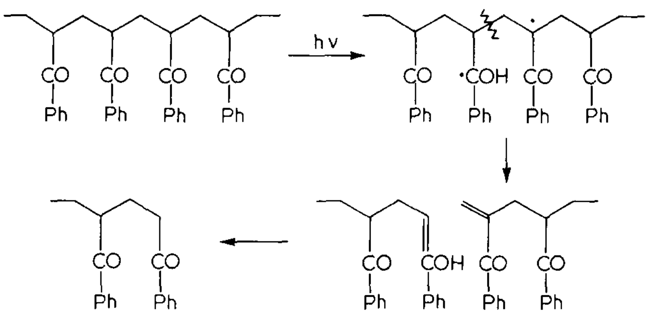

Scheme I

our study and also includes the values recently determined[16,18] for poly(*p*-methoxyacrylophenone) and related copolymers. With chlorobenzene as a solvent the temperature range accessible was not wide enough for suitable Arrhenius studies, but the lifetime of 225 ns measured at 244K is consistent with the values in other solvents. *Figure 1* shows the Arrhenius plot obtained in chloroform. We have frequently observed that the main decay process is preceded by a fast process responsible for a small fraction of the decay that depends upon the history of the sample. That is, the importance of the fast component increases when the sample has been exposed to u.v. light. We have proposed earlier[16] that the fast component observed in poly(*p*-methoxyacrylophenone) reflects the decay of those macromolecules that have incorporated quencher end-groups as a result of photodegradation reactions, since vinyl ketone moieties are known to be excellent triplet quenchers[5] (see Scheme I). All our decay measurements were carried out on the slow component which usually accounts for >80% of the decay; i.e. in a system where two distinct types of macromolecules are present (quencher-free and quencher-containing), our kinetic parameters refer exclusively to the quencher-free polymer. It seems likely that our use of a low molecular weight macromolecule has also facilitated the study of the slow component[6].

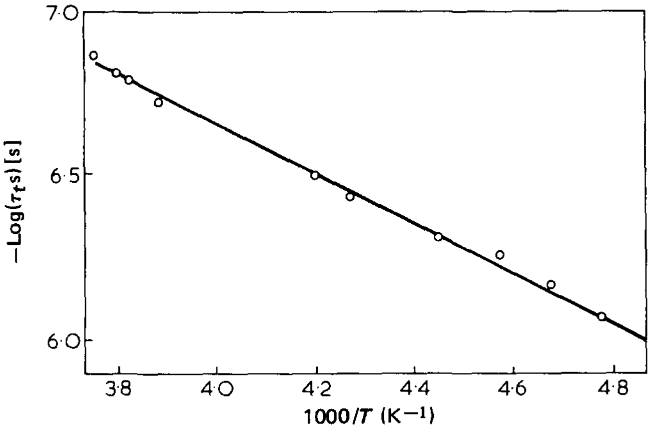

Figure 1 Arrhenius plot for the decay of PPVK in chloroform

To confirm our characterization of the triplet state a few quenching experiments were carried out using 1,3-octadiene as triplet quencher. In toluene at 231K we obtained $k_q = 5.1 \times 10^8$ M^{-1} s^{-1}, thus supporting our assignment.

Reported triplet lifetimes for PPVK at room temperature range from 7.5 ns[7] to 100 ns[4] with many other values distributed more or less randomly within this range. It is perhaps surprising that discrepancies of this magnitude still exist in a polymer that has been widely used as a model for ketone behaviour in macromolecules. Some of the differences are undoubtedly the result of the combination of good $k_q\tau_t$ values with assumed k_q values; however, we feel that in most cases the differences reflect true lifetime differences between samples of PPVK prepared and/or handled differently. That is, lifetimes determined by any technique that does not separate quencher-free and quencher-containing molecules are a composite of both types of decay. Our values at room temperature (*Table 1*), even if extrapolated, represent the lifetime of quencher-free macromolecules, and in this sense are a better measure of the kinetics of the Norrish Type II fragmentation.

The activation energies obtained for PPVK (3–3.6 kcal mol^{-1}) are substantially smaller than those measured for poly(*p*-methoxyacrylophenone)[16]. The difference is consistent with the expected unreactivity of the low lying π,π^* triplet in poly(*p*-methoxyacrylophenone)[16,19].

Table 1 Temperature dependence of the decay of triplet polymeric ketones[a]

Polymer	Solvent	Log A[b]	E_a[c]	τ_t (ns[d])	Ref.
PPVK[e]	Toluene-d_8	9.90 ± 0.50	3.56 ± 0.30	57	this work
PPVK	Chloroform	9.69 ± 0.62	3.14 ± 0.58	74	this work
PPMA[f]	Benzene	10.61	5.96	–	16
PPMA	Chlorobenzene	10.37	5.61	–	16
PPMA	Chloroform	9.99 ± 0.75	5.92 ± 1.11	2770	this work
Co(PMA–PVK)[g]	Benzene	10.62	5.46	–	16
Co(PMA–PVK)	Chloroform	10.84	6.03	–	16

[a] All errors correspond to 95% confidence limits
[b] With the pre-exponential factor in units of s^{-1}
[c] In kcal mol^{-1}
[d] At 20°C
[e] Poly(phenyl vinyl ketone)
[f] Poly(*p*-methoxyacrylophenone)
[g] Copolymer of *p*-methoxyacrylophenone (80%) and phenyl vinyl ketone (20%)

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