

Polymers with enhanced photostability: photoreactions of poly(*o*-isobutyrylstyrene) in the long-wave region

Neil A. Weir ^{*}, Jerzy Arct, Alfredo Ceccarelli, Kenneth Whiting

Chemistry Department, Lakehead University, Thunder Bay, Ont. P7B 5E1, Canada

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Abstract

Poly(*o*-isobutyrylstyrene) (POIS) was exposed in the solid state to long-wave UV radiation ($\lambda \geq 300$ nm) under high vacuum conditions at 25 ± 1 °C. Transient spectral measurements indicate the presence of two distinct enols, i.e. the *syn* and *anti*, which have lifetimes of 163 ns and 4.5 μ s respectively. The most important photoprocess is photoenolization, and although the *syn* carbonyl triplet is principally involved, experimental data indicate that the corresponding singlet may also contribute to the process. The *anti* carbonyl triplet appears to play a relatively passive part in photoenolization; however, it is involved in α -scission which leads to the formation of isopropyl radicals which, in turn, give rise to propane (principal product), propene and 2,3-dimethylbutane. Quantum yields for the formation of these products are low (10^{-5}), and this reflects the extent of competition from photoenolization. Similarly, the extent of cross-linking is very small. The carbonyl concentration is depleted to a minimal extent; thus, in terms of photodegradation, POIS appears to be a relatively photostable polymer.

Keywords: Photodegradation; Poly(*o*-isobutyrylstyrene); Photoisomerization; α -Scission

1. Introduction

The photophysics and photochemistry of *o*-alkylacetophenones have been studied extensively during the past two decades. These molecules undergo reversible photoenolization on irradiation in the long-wave region ($\lambda \geq 300$ nm), the biradicals formed by intramolecular H-abstraction rearranging rapidly to form the enols [1–7].

In the ground state these molecules exist as an equilibrium mixture of the *syn* (*Z*) and *anti* (*E*) conformers with respect to rotation about the aryl-(C=O) bond. On irradiation the $n \rightarrow \pi^*$ singlet states are formed, and these undergo rapid intersystem crossing (ISC) ($\Phi_{ISC} \rightarrow 1.0$) to form two kinetically distinct $n \rightarrow \pi^*$ triplets. The *syn* conformer has the appropriate geometry for intramolecular γ -H abstraction, and the corresponding biradical is formed rapidly (rate constants typically being 10^8 – 10^9 s⁻¹). However, the *anti* conformer is inappropriately oriented and must firstly undergo rotation into the *syn* conformation before H abstraction can occur. The rate of H abstraction is then controlled by the rate of bond rotation, the effective rate constant being typically 10^7 s⁻¹ [8,9]. Since conformational equilibrium is also established in the biradical, two distinct enols (*Z* and *E*) are also formed [10]. While the *Z*-enol can undergo rapid reketonization by

an allowed suprafacial [1,5] sigmatropic shift, the *E*-enol must undergo an intramolecular reaction which has not only a higher energy requirement but also a less favourable entropic contribution [5–7].

From the point of view of polymer photodegradation, and many keto polymers undergo rapid degradation, even in sunlight [11], such rapid, reversible photoenolization would be highly desirable since it would provide an alternative, independent route for the deactivation of the initially excited states. As a consequence, quantum yields for the degradative reactions would be significantly reduced, and if the time scale for reketonization were similar to that of the low molecular weight ketones, the keto moieties would be rapidly returned to their original chemical state.

A limited number of studies of photoenolization of keto polymers have been carried out; however, it has been established that *o*-methylbenzoyl moieties present in both homo- and copolymers undergo photoenolization [12,13] as do the poly(*o*-acylstyrenes) [14–16]. In both cases the keto groups are appropriately oriented for γ -H abstraction, and the resulting photoenolization competes very effectively with degradation.

The enhanced photostability of such polymers is exemplified by the two isomeric poly(acetylstyrenes) (i.e. *o* and *p*). In the latter case, the quantum yield for α -scission is about

^{*} Corresponding author.

two orders of magnitude greater than that for the *o* isomer. The advantages of polymers having enhanced photostability in the long-wave UV region are obvious in the fields of solar energy transfer and conversion in which degradation greatly impairs the efficiency of these processes [17,18].

The work described below is an extension of our investigations of potentially more photostable polymers. In this case the photophysics and photochemistry of poly(*o*-isobutyrylstyrene) (POIS) are studied.

2. Experimental details

2.1. Materials

The monomer was prepared and purified as described elsewhere [19]. Polymerization was carried out in bulk at 65 °C under high vacuum and in the presence of azobisisobutyronitrile (10^{-3} M). The degree of conversion was limited to 10%, and the polymer was precipitated in methanol and purified by standard methods [19].

2.2. Spectroscopic measurements

Both degraded and undegraded polymers were investigated by UV spectroscopy (Perkin Elmer Lambda 11), emission spectroscopy (Perkin Elmer LS50B) and ^{13}C nuclear magnetic resonance (NMR) spectroscopy (at 20.1 MHz in CDCl_3) (Brüker AM 300).

The ^{13}C NMR spectrum of the polymer was studied in detail on account of our interest in the geometry of the molecule and its potential effects on photoisomerization. Assignments are shown in Fig. 1, and it can be inferred that, in the ground state, the molecule exists predominantly in the *syn* conformation (i.e. approximately 85%).

2.3. Molecular weights

Molecular weights \bar{M}_n and \bar{M}_w and molecular weight distributions were determined by gel permeation chromatography (GPC) (Waters equipment with Ultrastaygel columns).

2.4. Photochemical techniques

Thin films (2×10^{-2} mm thick), which were cast on quartz plates by solvent evaporation (CH_2Cl_2), were exposed to

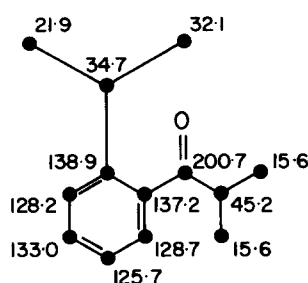


Fig. 1. ^{13}C NMR assignments for POIS (20.1 MHz in CDCl_3).

long-wave UV radiation ($\lambda \geq 300$ nm) under high vacuum (10^{-6} Torr (133×10^{-6} Pa)). The radiation source was a high pressure mercury arc (Hanovia 200 W), and the Pyrex reaction vessel restricted the wavelengths of the incident radiation to those of 300 nm and greater. The temperature was maintained at 25 ± 1 °C by circulating water (at 25 °C) through the annular space of the reaction vessel. Rates of absorption of long-wave quanta were determined by UV spectroscopy and quantum yields for the principal photoreactions were estimated by photochromic actinometry [20]. Similarly, the quantum yield for fluorescence was obtained, the absorption and emission characteristics of the polymer being compared with the standard data available for anthracene [21].

2.5. Laser flash photolysis and transient spectroscopy

Polymer solutions were degassed and irradiated with pulses of 8–10 ns duration (10 mJ at 337 nm) from a nitrogen laser (Moletron UV-24). A detailed description of the technique and of the associated detection systems has been published [22].

2.6. Analyses of gaseous products

Low molecular weight gaseous products were analysed quantitatively throughout the irradiation period, the reaction vessel being directly coupled to a quadrupole mass spectrometer (Dataquad 200). The dedicated microprocessor produced time evolution characteristics for all the volatile components in the range $1 \text{ amu/e}^- < m/e < 150 \text{ amu/e}^-$. The equipment is described in detail elsewhere [23].

3. Results

3.1. UV and emission spectra

The UV absorption spectrum (thin film) shown in Fig. 2 resembles those of other *o*-substituted styrene polymers and also those of low molecular weight *o*-alkylacetophenones in that the most intense absorption occurs in the short-wave region, the two maxima being associated with symmetry-forbidden $\pi \rightarrow \pi^*$ transitions of the aromatic moiety (i.e. $^1\text{A}_{1g} \rightarrow ^1\text{B}_{2u}$ and $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1u}$). The less intense long-wave band ($\lambda_{\text{max}} = 320$ nm) is due to the $n \rightarrow \pi^*$ transition of the carbonyl group which is the only chromophore of interest to the present work. On account of the relatively low value of the absorption coefficient at 320 nm (i.e. $\epsilon = 130 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and the small film thickness, the extent of attenuation of the long-wave UV radiation by the films is minimal.

Vacuum irradiation does not produce any measurable changes in the carbonyl concentrations, and no new long-wave-absorbing species were formed.

The fluorescence spectrum (together with the exciting spectrum) is also shown in Fig. 2. It can be seen that there is

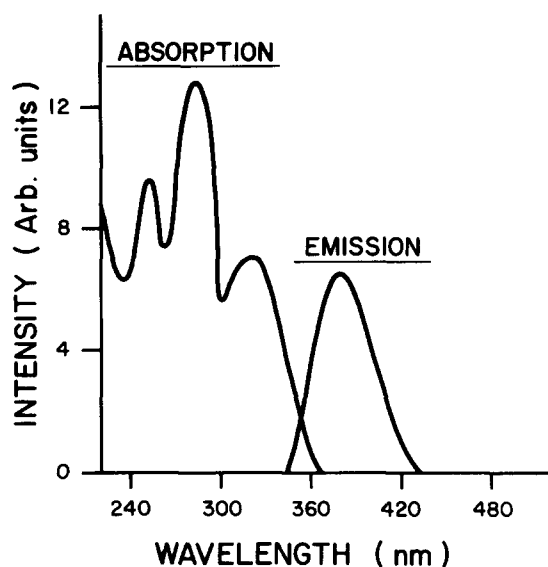


Fig. 2. Absorption and emission spectra of POIS film (2×10^{-2} mm thick).

a single emitting species ($\lambda_{\max} = 380$ nm) and the quantum yield is about 10^{-4} . The spectrum exhibits mirror image characteristics in the long-wave region, and the magnitude of the Stokes shift is small indicating close similarities between the geometries of the ground and the first excited singlet $\pi \rightarrow \pi^*$ states [24,25].

3.2. Transient spectra

Laser excitation of degassed solutions of the polymer (in CH_2Cl_2) produced a new absorption in the 390–400 nm region, and this was due to transient species. A study of the time decay characteristics of the transient absorption showed that there were two distinct species formed, one short and the other considerably longer lived. The time-resolved decay characteristics are shown in Figs. 3 (short lived) and 4 (long lived) (some of the data points have been omitted for clarity).

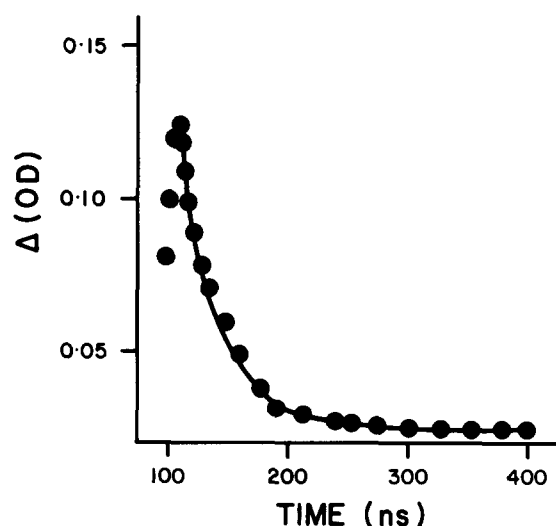


Fig. 3. Decay characteristics of the short-lived enol formed from POIS monitored at 390 nm).

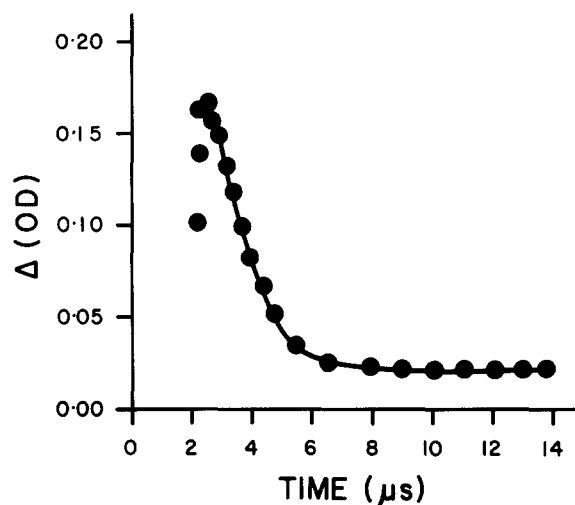


Fig. 4. Decay characteristics of the long-lived enol from POIS (monitored at 390 nm).

There is a good correlation between these experimental data and the expected exponential decay characteristics, and lifetimes of $163 \text{ ns} \pm 10\%$ and $4.5 \mu\text{s} \pm 10\%$ can be derived from the data.

Although the yields of the transients were reduced considerably by the addition of standard triplet quenchers (e.g. *cis*-1,3-pentadiene), the overall quenching efficiency was less than 100%, and the Stern–Volmer data were non-linear. It is clear that the triplet is involved in the photoisomerization, but the above observations indicate the additional participation of the singlet state [26]. Similar evidence for the participation of the biradical was obtained, the product of reduction of paraquat (PQ^{2+}), i.e. PQ^+ , being detected by its specific absorption at 603 nm. Biradical lifetime determination was greatly complicated by the differential solubilities of the polymer and PQ^{2+} , the latter being only sparingly soluble in “good” solvents for the polymer. However, the lifetime of the biradical was estimated to be of the order of 200–300 ns.

3.3. Low molecular weight products

The most abundant product was propane; however, smaller amounts of propene, 2,3-dimethylbutane and trace amounts of CH_4 and CO were also formed. Typical time evolution characteristics of propane formation are shown in Fig. 5. The data are qualitatively very similar to what were obtained for other similar polymers [15,16,18]. The quantum yield Φ_X of a product X is given by the relation

$$\Phi_X = \frac{d[X]/dt}{I_a}$$

in which I_a is the rate of absorption of long-wave ($\lambda \geq 300$ nm) quanta by the film and $d[X]/dt$ is the rate of formation of the product. I_a is further defined as

$$I_a = AI_0[1 - \exp(-\beta L)]$$

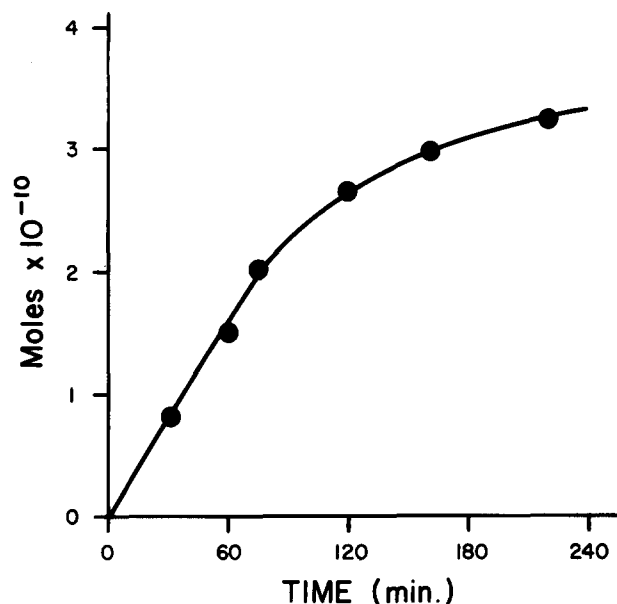


Fig. 5. Time evolution characteristics of propane, the principal photoproduct of POIS (irradiation at $\lambda \geq 300$ nm under high vacuum at 25 °C).

Table 1

Quantum yields for formation of low molecular weight products from poly(*o*-isobutylstyrene) (irradiation at $\lambda \geq 300$ nm under high vacuum)

Product X	$\Phi_X \pm 10\%$ (mol einstein ⁻¹)
CO	$< 10^{-6}$ (trace)
CH ₄	$< 10^{-6}$ (trace)
C ₃ H ₆	1.9×10^{-5}
C ₃ H ₈	3.3×10^{-5}
C ₆ H ₁₄	1.7×10^{-5}

in which A is the area of film irradiated, L is its thickness, I_0 is the incident radiation flux and β is the absorption coefficient of the film (β is equivalent to ϵC (C is the concentration) as used in solutions). Since both β and L are small, the quantum yield for X formation can be approximated as

$$\Phi_X = \frac{d[X]/dt}{I_0\beta AL}$$

Quantum yields for all the gaseous products are shown in Table 1.

3.4. Other spectral changes

Small qualitative differences were observed in the spectra of degraded polymers; for example, the C=O absorption (1685 cm^{-1}) and the ¹³C NMR signals at 200.7 ppm (due to the C=O) and at 15.6 ppm (due to the alkyl group) decreased in intensity. However, the differences were too small to be of quantitative (or mechanistic) significance. Together with the quantum yield data, these results would indicate that the principal degradative reaction involves α -cleavage.

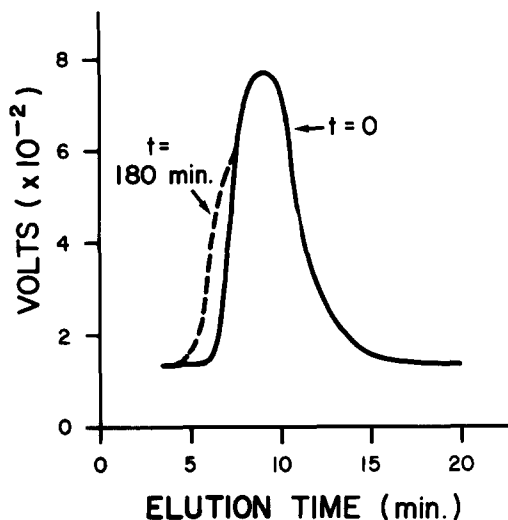


Fig. 6. Change in molecular weight distribution following irradiation of POIS for 3 h ($\lambda \geq 300$ nm under high vacuum) (GPC data).

3.5. Molecular weight data

Changes in molecular weight as indicated by GPC data are shown in Fig. 6. There is no evidence for chain scission, but some higher molecular weight material is formed, presumably as a result of cross-linking. These changes are much smaller than those observed for the isomeric *para*-substituted polymers [27].

4. Discussion

4.1. Primary and photophysical processes

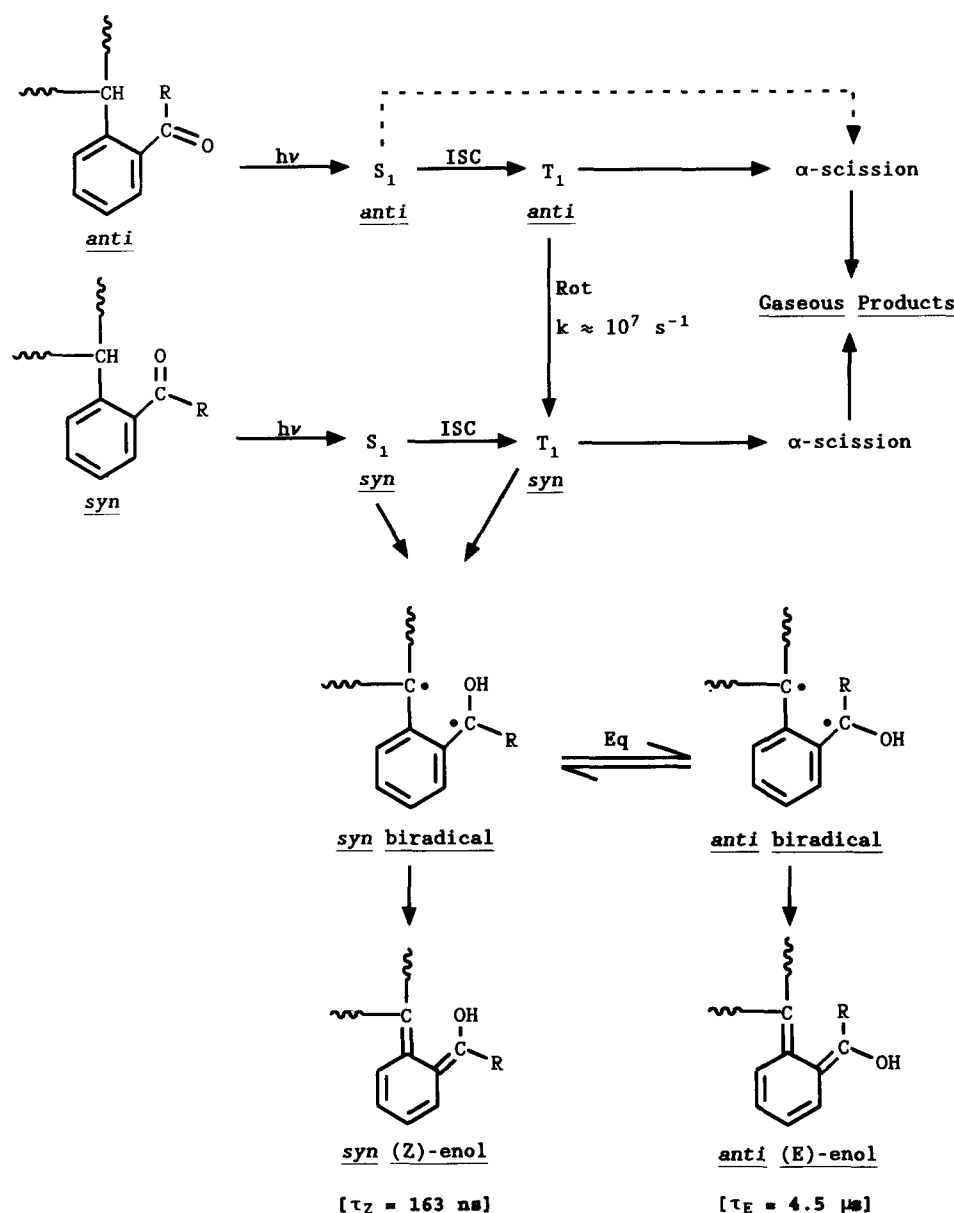
The initial excited species formed on absorption of long-wave quanta is the $n \rightarrow \pi^*$ singlet which can be deactivated by a number of photophysical processes including internal conversion, fluorescence, which has been observed (Fig. 2), and by ISC which in the case of aromatic carbonyls like this occurs both rapidly and in high quantum yield [26,28]. In the case of the lower molecular weight *o*-alkyl aromatic carbonyls, the major part of the photochemistry, including photoisomerization, derives from the n, π^* triplet states. Experimental data, however, would suggest that this is not necessarily so in the case of POIS. That the addition of well-known triplet quenchers does not completely suppress the formation of products, together with the non-linear Stern–Volmer behaviour, would imply that the triplet is not the only excited species involved. Indeed, the fact that fluorescence is observed, admittedly in low quantum yield, indicates that the singlet could also participate, particularly in fast reactions. In addition, other studies have shown that rates of γ -H abstraction (which is a prerequisite for enolization in POIS) by carbonyl n, π^* singlets are not only greater than those from the corresponding triplets but also comparable and, in some cases, even greater than the rates of ISC [5,10,21,28].

It could be argued, however, that the quenching process itself is inefficient, energy transfer from the excited carbonyl occurring by the exchange mechanism which requires close contact between the orbitals of the carbonyl and the quencher. In POIS access to the carbonyl may be restricted by the adjacent polymer chain in which case the orbital interaction is reduced. Steric restriction of quenching efficiencies is certainly not unknown [29–31]. A similar explanation could be offered for the inconclusive results of the trapping experiments (with PQ^{2+}).

The principal reaction of POIS is photoenolization, intramolecular (γ) H abstraction leading to the formation of a biradical which subsequently rearranges to the enol [2,5,6]. In the ground state of POIS there are two conformationally

distinct keto species, i.e. *syn* and *anti*, and our NMR measurements indicate that the *syn* conformer is the predominant species (at least 80%). Absorption of UV quanta produces initially two conformationally distinct n,π^* singlet states which can undergo ISC to form two triplets.

While the carbonyls in the *syn* conformation (both singlet and triplet) are appropriately oriented to undergo rapid γ -H abstraction to form the biradical, the *anti* conformer must first of all undergo rotation into the *cis* form from which it can react. This has two major consequences. On account of the relative magnitudes of the rate constants for acyl group rotation (typically 10^7 s^{-1}) and those for γ -H abstraction (in the 10^8 – 10^9 s^{-1} range), rotation will become the rate-determining step for *anti* carbonyl participation in H abstraction



Scheme 1.

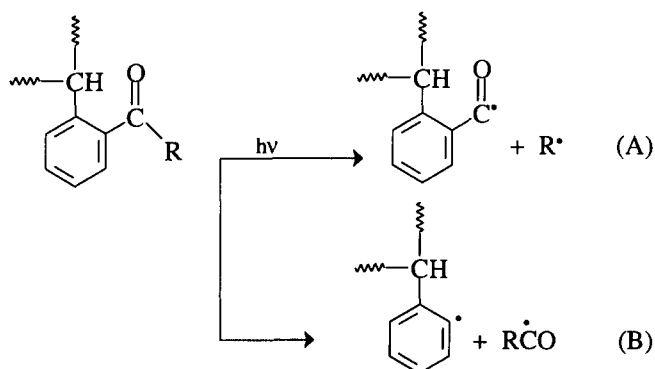
[8,28]. In addition, ISC to the *anti* triplet (rate constant typically in 10^8 – 10^9 s $^{-1}$ range) will be complete before rotation can occur [8,21,28]. Thus the *anti* singlet will not be involved in enolization, and any *anti* triplet participation will be rotationally controlled and hence probably insignificant.

This does not imply that the *anti* enol cannot be formed since experimental evidence clearly indicates the reverse. Conformational equilibrium can be established in the biradical, the lifetime of the POIS biradical (estimated at 400 ns) being sufficiently long for this to occur [10].

The very large differences in lifetimes of the *Z*- and *E*-enols can be rationalized in terms of the ease, or otherwise, of reketonization. In the case of the *Z*-enol, this involves an allowed suprafacial [1,5] sigmatropic shift which has a relatively low energy requirement. On the contrary, reketonization of the *E*-enol involves H abstraction from a more distant C atom, and this has not only a larger energy of activation but also a lower or negative entropy of activation [5]. The reactions involved in photoisomerization are summarized in Scheme 1.

4.2. Other photoprocesses

The nature of the low molecular weight products clearly indicates that α -scission (Norrish type I) is occurring, geminate radical pairs being formed initially. Two possible scissions may occur ($R = \text{iso-C}_3\text{H}_7$), i.e.



On the grounds of relative radical stabilities, scission (A) would appear to be more likely, and this is confirmed by the products, most of which can be associated with combination, disproportionation and H abstraction by isopropyl radicals. In addition, the relatively very low quantum yield for CO formation would indicate that these radicals are not derived from the acyl radical formed in scission (B). The presence of methane would suggest that scission β to the carbonyl also occurs to a small extent. This type of reaction is not unknown in the photochemistry of low molecular weight ketones, and, since the fission is not energetically favourable, the quantum yields are characteristically low [32].

The generally low quantum yields for gas evolution, and hence for α -fission, reflect the very large amount of competition from photoisomerization, and while both *syn* singlet and triplet states can participate readily, carbonyls in the *anti*

conformation would appear to adopt a relatively passive role. They can, however, undergo α -fission. On the basis of symmetry correlations [33] and recent observations of aromatic ketones [28], α -fission is more likely to originate from the *anti* triplet, the rate constant for the corresponding reaction from the singlet being not only typically two orders of magnitude lower but also lower than that for ISC [21]. Thus, while the *anti* triplet plays a major role in the photodecomposition of POIS, the involvement of the *syn* triplet cannot be excluded. The magnitudes of the relevant rate constants (for α -H abstraction, leading to biradical formation and for α -fission) are not known; however, quantum yields for α -fission in the isomeric *para*-acylstyrene polymers, in which triplets are exclusively involved, are at least two orders of magnitude greater than those obtained for POIS (Table 1) [14]. It is therefore reasonable to suggest that the extent of α -fission occurring from the *syn* triplet is relatively minor.

These conclusions have important implications in the photodegradation of such polymers. The photostability of a polymer can be enhanced by reducing the concentration of the *anti* conformer (e.g. by increasing the complexity of the R substituent) in which case the absorbed energy can be dissipated principally in enol formation.

4.3. Secondary reactions

The gaseous products result from the reactions of isopropyl radicals, combination and disproportionation respectively, giving rise to 2,3-dimethylbutane and propane and propene. On the basis of previous investigations, propane can also be formed by H abstraction from the polymer, the most probable reaction site being the α -C atom [34].

Molecular weight increases may be attributed to cross-linking, macroradicals formed by α -fission and those resulting from H abstraction from the polymer being involved. The low rate of crosslinking (cf. *p*-substituted acylstyrenes) [14] reflects the lower concentration of macroradicals. However, cross-linking is also subject to adverse steric effects; radical centres, particularly those formed by α -fission, are considerably shielded by the adjacent polymer chains.

Acknowledgments

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