Photoreactions of poly(α-methylvinylacetophenone) in solution

N. A. Weir*, A. Ceccarelli and J. Arct
Chemistry Department, Lakehead University, Thunder Bay, Ontario P7B 5E1, Canada
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Dilute solutions of poly(α-methylvinylacetophenone) (PMVAP) were exposed to long-wave ($\lambda \geqslant 300$ nm) u.v. radiation under high vacuum conditions. The low molecular weight products, analysed by mass spectrometry, were ethane, methane and CO, and their appearance indicates that PMVAP decomposes via Norrish type I (α cleavage) reactions. The relatively higher ethane yield reflects the greater difficulty of H abstraction by methyl radicals, substitution at the α-C atom forcing the methyls to abstract at the less reactive secondary C atoms. Random chain scission also occurs, and has been attributed to the β scission of macroradicals, which are formed by abstraction reactions involving methyl radicals, and more importantly, carbonyl triplets (photoreduction). Spectroscopic evidence supports the proposed chain scission mechanism.

(Keywords: poly(α-methylvinylacetophenone); photolysis; long-wave u.v.; Norrish type I reaction; photoreduction; chain scission)

Introduction

Considerable interest has been shown in poly(vinylacetophenone) (PVAP) as a solar energy transfer material[1]. It does, however, suffer from the disadvantage of undergoing concomitant photodegradation on exposure to long-wave u.v. radiation ($\lambda \geqslant 300$ nm), and attempts have been made to reduce its photodegradability, while at the same time retaining its favourable optical and energy transfer properties.

To this end, we have synthesized and studied the photochemistry of films of poly(α-methylvinylacetophenone) (PMVAP), and have shown that it has significantly greater photostability than PVAP, substitution at the α-C atom reducing the probability of abstraction, and as a consequence, the rates of production of methane and of radical centres on the chains. The polymer does, however, undergo crosslinking, and the resulting insolubilization complicates investigations of its photochemistry, in particular those reactions involving molecular weight changes.

In the work described here, a parallel study of the photochemistry of PMVAP was carried out in dilute solution, in which medium cage effects are less significant, and crosslinking, though not eliminated, is at least delayed.

Experimental

Polymer preparation. Poly(α-methylstyrene) (Polysciences Standard: molecular weight, $\bar{M}_n = 90 \times 10^3$ and $\bar{M}_w/\bar{M}_n = 1.1$) was acetylated using a procedure previously described[2]. The polymer was isolated by precipitation, the solution of crude material (in dichloromethane) being added to pure methanol. The process was repeated three times, after which the polymer was dried at 50°C under high vacuum. The degree of acetylation was at least 95%, and this was confirmed by comparing values of the integrations of the ^{1}H n.m.r. spectrum (250 MHz), in particular the relative intensities of signals at 7.75 ppm (aromatic protons) and at 2.58 ppm (acetyl group protons).

Photochemical techniques. PMVAP solutions (6×10^{-2} M) were thoroughly degassed by alternate freezing and thawing under high vacuum (10^{-6} torr; 1 torr = 0.13 kPa), and were irradiated under similar conditions, the solvent being dichloromethane. Samples were exposed at 25 ± 1°C to the filtered (Corning type 9-53) output of a medium pressure Hg arc (Hanovia 200 W), the incident radiation having wavelengths $\geqslant 300$ nm. Details of the equipment and techniques are published elsewhere[3].

Analytical measurements. The progress of the reactions was followed by molecular weight measurements, by gas analyses and by spectroscopic analyses of the polymer residue. Number average molecular weights were carried out using gel permeation chromatography (Waters) with CH_2Cl_2 as solvent. Samples were withdrawn from the reaction vessel at regular intervals, and injected into the columns (Ultrastyragel). The equipment was calibrated with narrow range molecular weight samples of poly(α-methylstyrene). Low molecular weight volatile products were analysed by a quadrupole mass spectrometer, as previously described[3], and i.r. and n.m.r. analyses were carried out using an *FT*i.r. spectrometer (Bruker IFS 66) and n.m.r. spectrometer (Bruker AM 300).

Results

The u.v. spectrum of a solution (6×10^{-2} M) of PMVAP closely resembles that of a thin film[4], in that the absorption in the long-wave (solar) region ($\lambda > 300$ nm) is restricted to that of the low intensity, symmetry forbidden $n \rightarrow \pi^*$ transition of the carbonyl[5] ($\lambda_{max} = 315$ nm, $\varepsilon = 45$ dm^3 mol^{-1} cm^{-1}).

Irradiation leads to a depletion of chromophore concentration; this is illustrated in *Figure 1*, in which the ratios of the intensities of the i.r. absorptions at 1685 cm^{-1} (carbonyl stretching frequency) and at 700 cm^{-1} (due to the aromatic moieties, and hence

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*To whom correspondence should be addressed

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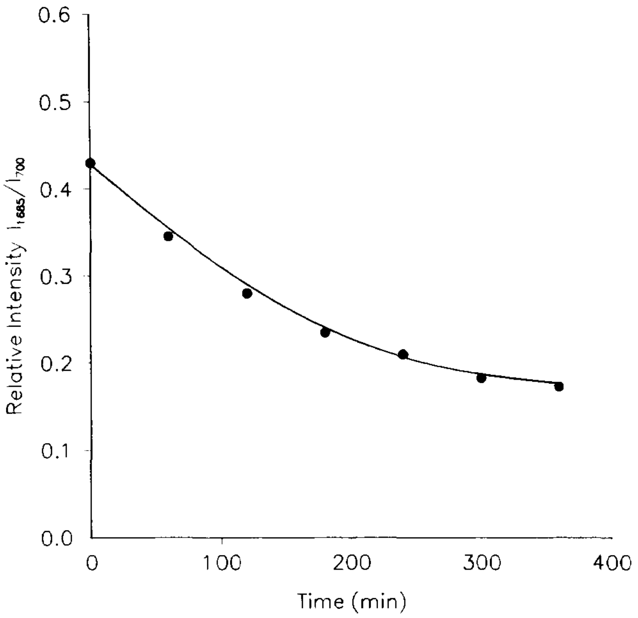


Figure 1 Ratio of i.r. intensity at 1685 cm^{-1} to that at 700 cm^{-1} as a function of time of irradiation of PMVAP solution (6 × 10^{-2} M) under high vacuum ($\lambda \geqslant 300$ nm)

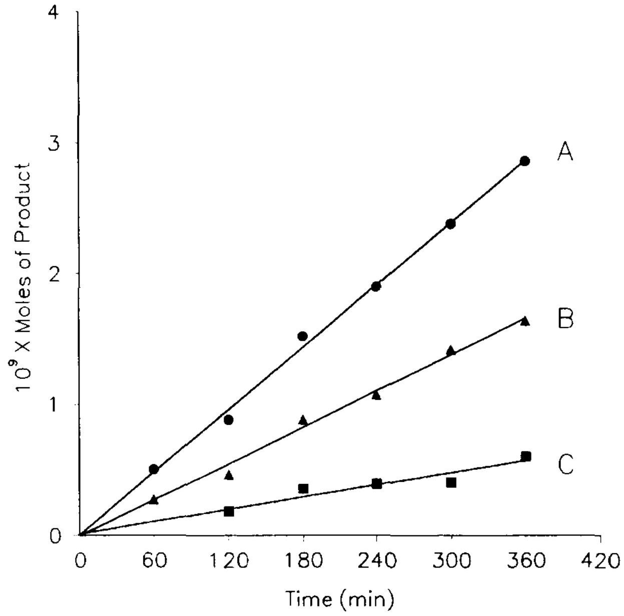


Figure 2 Time evolution characteristics of low molecular weight products from the photolysis of PMVAP solution (6 × 10^{-2} M) under high vacuum ($\lambda \geqslant 300$ nm): A, C_2H_6; B, CH_4; C, CO

invariant during irradiation), i.e. I_{1685}/I_{700}, are shown as a function of time of exposure. Other i.r. spectral changes include the appearance of a new peak at 3460 cm^{-1} and a lower intensity, less structured absorption around 1600 cm^{-1}. N.m.r. spectral changes at 197 ppm in the ^{13}C spectrum, and at 2.58 ppm in the ^1H spectrum, confirm that decomposition of the acetyl group is occurring, and this is accompanied by the appearance of a new peak at 5.3 ppm.

The characteristics of volatile product formation are shown in *Figure 2*, and they are qualitatively similar to those observed for the irradiation of films of PMVAP[4]. They do, however, differ significantly from those obtained

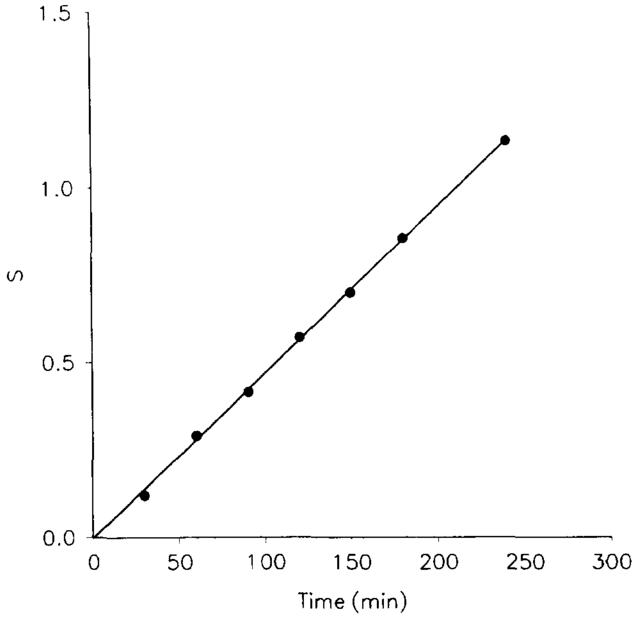


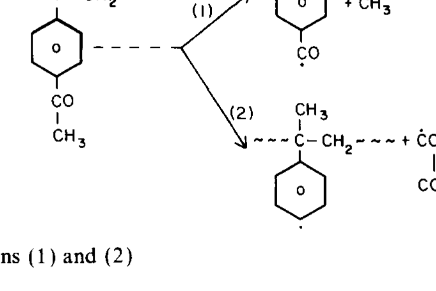
Figure 3 Number of chain scissions per molecule, *S*, as a function of time of irradiation of a solution of PMVAP (6 × 10^{-2} M) under high vacuum ($\lambda \geqslant 300$ nm)

for PVAP[3], in that the relative abundances of methane and ethane are reversed (CH_4 is the main product from PVAP).

Irradiation also results in a decrease in molecular mass, the linear time dependence (*Figure 3*) implying that random chain scission is occurring. In this respect, the present results differ most significantly from those observed for PMVAP films, in which crosslinking predominates[4].

Discussion

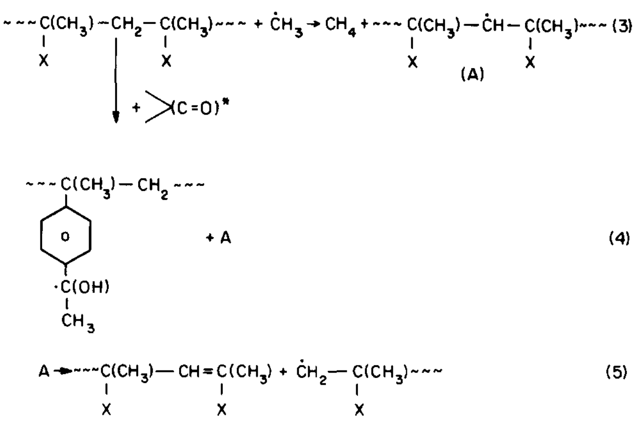
The nature of the gaseous products clearly indicates that like PVAP, PMVAP undergoes α cleavage (Norrish type I reactions) on long-wave irradiation. Although two fission processes are possible (reactions (1) and (2)), the relative abundances of CO and hydrocarbon products suggest that reaction (1) is the more probable, and this can be reconciled with the relative stabilities of the macroradicals which result from the two fissions.



Reactions (1) and (2)

As in the case of solid PMVAP samples, the ethane yield exceeds that of methane, and this reflects the greater difficulty of abstraction from PMVAP, the methyl radical being forced, on account of α substitution, to abstract at secondary C atoms, at which the dissociation energies of C–H bonds are higher[6,7].

Chain scission in polymers like PMVAP can be accounted for in terms of β scission in macroradicals which are formed by H atom abstraction from C atoms in the chains, and this can be brought about not only by interactions with methyl radicals, but also by reactions of the carbonyl triplets (photoreduction)[3,8,9]. Random chain scission may be represented by the reaction sequence (3)–(5):



in which X = $PhCOCH_3$

Though energetically less favourable, H abstraction at the α-methyl group is not excluded, and β scission of the resulting radical would also give rise to chain scission.

A comparison of the CH_4 yield and the extent of chain scission would suggest that, as in other cases, photoreduction is the main source of A radicals[10]. Both inter- and intramolecular photoreductions are possible, and these are facilitated by the greater flexibility and rotational freedom available in the dilute solution, specific conformational requirements for H abstraction being more readily achievable than in the solid state, in which only crosslinking is observed[4]. According to reactions (4) and (5), chain scission should be accompanied by the formation of hydroxylic and unsaturated species. The fact that independent spectroscopic evidence for both was obtained – i.e. the i.r. indicated the formation of unsaturated species and the photo-enol, and the new peak at 5.3 ppm in the ^1H n.m.r. spectrum indicated the presence of the $-CH=$ moiety – lends some support to the proposed mechanism of chain scission.

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