

Preliminary Note

Trapping by methyl methacrylate of the biradicals derived from the photolysis of some alkyl aryl ketones: A novel initiation of polymerization

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A few experiments describing the trapping of the biradicals which result from the intramolecular photochemical γ -hydrogen abstraction in ketones undergoing the Norrish type II process have been reported in the last few years [1 - 3]. Mercaptans [1] and oxygen [2] in solution, as well as hydrogen bromide in the gas phase [3] are efficient scavengers of these biradicals. O'Neal *et al.* have been able to estimate the lifetime of the biradical derived from pentane-2-one as $10^{-4.9}$ s at 388 K, the value being consistent with the reactivity observed in the experiments in solution [1, 2, 4]. The relatively long lifetime of these biradicals suggests that they should be able to undergo some bimolecular reactions characteristic of free radicals; among these, the addition to vinyl monomers can be expected to be of considerable importance.

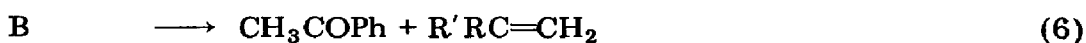
We have examined the photolysis of acetophenone, butyrophenone, valerophenone and isocaprophenone in neat methyl methacrylate. The experiments were designed to examine the possibility of initiating vinyl polymerization by 1,4-biradicals. The results of a series of experiments are summarized in Table 1. Acetophenone, being unable to generate biradicals, and in the absence of good hydrogen donors decreases the yield of polymer formation. This effect can be attributed to the absorption of light by acetophenone, which in its absence would be, to some extent, absorbed by the monomer. This monomer absorption results (at least partly) in the initiation of radical polymerization, directly or *via* trace impurities. In the presence of tetrahydrofuran as a hydrogen donor acetophenone behaves as a free radical initiator, as expected [6]. Considering the three ketones bearing γ -hydrogen atoms the quantum yields of polymerization show the following trend: isocaprophenone > valerophenone > butyrophenone.

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Clearly, the quantum yield is higher the shorter the triplet lifetime [5]; on the other hand, acetophenone, having the longest triplet lifetime, but no possibility of producing biradicals leads to the lowest quantum yield. Since all the ketones can be expected to show similar reactivities in bimolecular reactions* and that therefore the triplet lifetimes (see Table 1) would lead to an inverse order, we are forced to conclude that the carbonyl triplet is not the species initiating the polymerization process.

We believe that the only reasonable explanation for these results is that the biradicals derived from γ -hydrogen abstraction are able to add to the monomer initiating the polymerization reaction. Further, the monomer should behave as a triplet quencher; this leads to a lower yield for biradical production for the ketones having longer triplet lifetimes. This is supported by the well known quenching ability of olefins, as well as by the low quantum yield of acetophenone production observed.

The following kinetic scheme is proposed:



from which:

$$R_9 = \frac{k_3 k_9 I_a [M]}{\{k_3 + (k_4 + k_5)[M]\} \{\tau_B^{-1} + k_9 [M]\}} \quad (10)$$

where K stands for a ketone bearing γ -hydrogen atoms ($\text{R}^1\text{R}^2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{Ph}$), B for a 1,4-biradical of the type $\text{R}^1\text{R}^2\dot{\text{C}}\text{CH}_2\text{CH}_2\dot{\text{C}}(\text{OH})\text{Ph}$, M for the monomer, I_a for the absorbed light intensity, τ_B^{-1} for $(k_6 + k_7 + k_8)$ and R_9 is the rate of reaction (9). Equation (10) shows that the process should be more efficient the higher the values of k_3 and k_9 and less efficient the faster the quenching reaction (4). If $(k_4 + k_5)$ could be neglected, then, the value of k_3 (*i.e.* τ_T^{-1}) would be irrelevant. k_5 is expected to be very small, otherwise, acetophenone would be an efficient initiator.

Several possibilities can be proposed for the chain propagation and termination steps.

*They are quite similar from the point of view of triplet energy, nature of the excited state and substitution at the carbonyl centre.

TABLE 1
Summary of experimental results

Ketone	Conversion ^a (%)	$[\eta]$ (dl/g)	$M_v \times 10^{-6}$	Φ_{ACP}^b	τ^c (s)
None	4.7	2.14	1.16	—	—
Acetophenone (ACP)	2.2	2.01	1.07	—	—
Butyrophenone	5.5	0.99	0.42	≤ 0.015	1.17×10^{-7}
Valerophenone	6.7	0.87	0.36	0.022	7.59×10^{-9}
Isocaprophenone	10.2	1.05	0.46	0.078	1.91×10^{-9}
ACP/THF ^d	4.3	1.79	0.92	—	—

^a 2 h reaction, 35°. ^b Measured by g.l.c. using the production of acetophenone from butyrophenone in benzene solvent as an actinometer. ^c From ref. [5] at 20 °C.

^d As in the experiment in line 2 in this Table but with 4% tetrahydrofuran (THF) added.

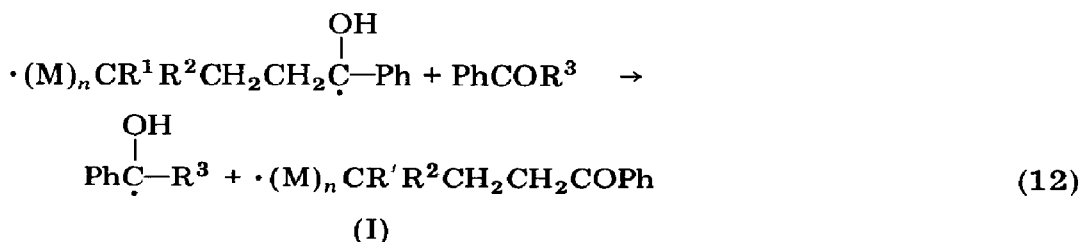
(a) The biradical $\cdot BM \cdot$ grows at both ends. The termination probably occurs mainly by the reaction:



Reaction (11) would lead to considerably high molecular weights. The results in Table 1 suggest that this mechanism is not operative.

(b) The propagating species continues to be a biradical, but only one end is reactive, the ketyl end being probably the unreactive one (see ref. [6]). Again, this mechanism would lead to high molecular weights, at least if the "active end-inactive end" termination by coupling is important. If the termination occurs mainly *via* disproportionation the interpretation of the data would be rather difficult.

(c) Either $\cdot BM \cdot$ or a biradical containing only a few monomer units transfers a hydrogen atom from the ketyl end, *i.e.*



The radical (I) follows then a conventional free radical polymerization mechanism. The ketyl radical probably behaves as a termination counterpart for the growing polymer radical in a mode similar to that proposed for the polymerization initiated by benzophenone-tetrahydrofuran mixtures. This mechanism is expected to lead to normal to low molecular weights and to incorporate aromatic carbonyl groups to the polymer structure.

At the present stage we feel that mechanism (c) is likely to be correct. However, a detailed kinetic study will be required to establish definitely the way in which the polymerization proceeds.

Although the participation of biradicals in vinyl polymerization has been invoked [7] in a few cases, we believe that this is the first time in which it has been definitely established that at least they must be involved in the initiation process and in the early stages of propagation*.

Experimental

Irradiations were carried out in a merry-go-round apparatus using a Phillips 250 W medium pressure mercury arc as light source (in a Pyrex housing). The samples (under nitrogen) were contained in matched Pyrex tubes and the concentration of ketone was high enough to guarantee over 99.5% light absorption at 313 and 366 nm. We feel that these are optimum conditions to check the trapping of the biradicals by the monomer; however, it should be noted that the radical concentration is inhomogeneous and time dependent (as the merry-go-round rotates) and the results cannot be used for kinetic studies.

Molecular weights were determined in benzene solvent at 30 °C from the intrinsic viscosity using the equation [9]:

$$\log \bar{M}_v = (\log [\eta] + 4.28)/0.76 \quad (13)$$

Quantum yields of acetophenone production were determined by gas-liquid chromatography (g.l.c.) using the photolysis of butyrophenone in benzene as an actinometer and n-dodecane as an internal standard.

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- 1 P. J. Wagner and R. C. Zepp, *J. Am. Chem. Soc.*, **94** (1972) 287; P. J. Wagner, P. A. Keslo, A. E. Kemppainen, J. M. McGrath, H. N. Schott and R. G. Zepp, *J. Am. Chem. Soc.*, **94** (1972) 7506.
- 2 J. Grotewold, C. M. Previtali, D. Soria and J. C. Scaiano, *JCS Chem. Commun.*, (1973) 207.
- 3 H. E. O'Neal, R. G. Miller and E. Gunderson, *J. Am. Chem. Soc.*, **96** (1974) 3351.
- 4 P. J. Wagner and K.-C. Liu, *J. Am. Chem. Soc.*, **96** (1974) 5952.
- 5 J. Grotewold, D. Soria, C. M. Previtali and J. C. Scaiano, *J. Photochem.*, **1** (1972/73) 471.
- 6 H. Block, A. Ledwith and A. R. Taylor, *Polymer*, **12** (1971) 271.
- 7 M. Hagiwara, H. Okamoto, T. Kagiya and T. Kagiya, *J. Polym. Sci. (A-1)*, **8** (1970) 3295.
- 8 R. K. Waring and G. J. Sloan, *J. Chem. Phys.*, **40** (1964) 772.
- 9 E. Cohn-Ginsberg, T. G. Fox and H. F. Mason, *Polymer*, **3** (1962) 97.

*An association or polymerization of Chichibabin's hydrocarbon has also been reported [8].