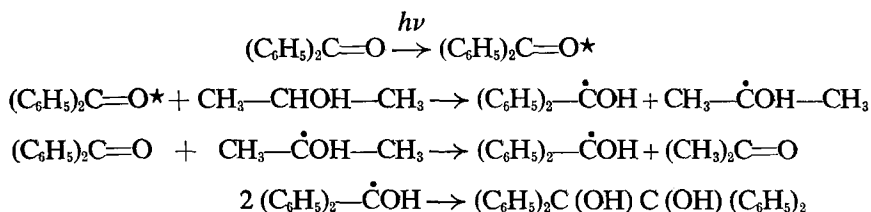


Photolysis of Polyvinylbenzophenone

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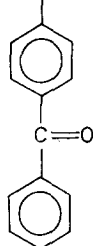
Photoreduction occurs when polyvinylbenzophenone (PVB) is irradiated at 3 650 Å. Recombination of the formed radicals leads to cyclization when polymer is irradiated in dilute solutions and to crosslinking in concentrated solutions and solid films. Absorption and emission spectra of the polymer and inhibition of the above reactions by naphthalene indicates that these proceed by a triplet state mechanism. The results obtained for PVB are compared with those of a model compound, p-propylbenzophenone.

PHOTOCHEMISTRY of benzophenone has been extensively investigated¹. In the presence of isopropanol photoreduction occurs leading to benzpinacol and acetone with quantum yields reaching unity.



The reaction proceeds through the $n-\pi^*$ triplet state of benzophenone and is inhibited by naphthalene in consequence of energy transfer. Other compounds can also act as hydrogen donor; with toluene a mixture of products is formed resulting from mutual and cross-recombination of ketyl and benzyl radicals².

The present work is concerned with the photochemical behaviour of polyvinylbenzophenone (PVB) $(-\text{CH}_2-\text{CH}-)_n$ irradiated at 3 650 Å in solid



state and in solution. Like polyphenylvinylketone, that has been recently studied³, this polymer has a phenylketone group but no labile hydrogen in the γ position relative to the carbonyl group. Photoreduction of PVB is expected to give rise to cyclization if the recombining radicals belong to the same macromolecule and to crosslinking if they are situated on different chains. Moreover breaking of the polymer chain could also occur. Photoreduction of a model compound, *p*-propylbenzophenone, was thus under-

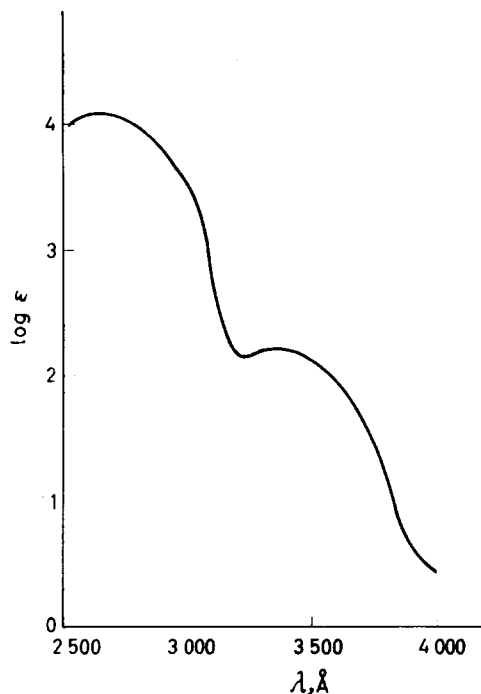
taken in order to elucidate the role of the side chain in the mechanism of the reaction.

EXPERIMENTAL

(1) *Synthesis and characterization of PVB*

PVB used in the photolysis experiments was obtained by reaction of benzoyl chloride on polystyrene in the presence of aluminium chloride⁴. Two samples A and B were prepared corresponding to benzylation yields of 83 and 92 per cent determined by absorption spectroscopy at 3 650 Å; their limiting viscosity numbers in benzene at 25°C were respectively 1 and 0.5 dl.g⁻¹. The absorption spectrum of pure PVB (*Figure 1*) was recorded

Figure 1—Absorption spectrum of PVB in chloroform at room temperature



using a sample synthesized by polymerization of vinylbenzophenone. The monomer was obtained by pyrolysis of benzoylated polystyrene and subsequent purification by distillation of the resulting oil under 10^{-5} mm Hg pressure. The phosphorescence spectrum of a PVB film irradiated at 77°K with 3 650 Å light is reproduced in *Figure 2*.

(2) *Synthesis and characterization of p-propylbenzophenone*

p-Propylbenzophenone was obtained by reaction of benzoyl chloride on propylbenzene in the presence of aluminium chloride⁶. Its phosphorescence spectrum in ethanol at 77°K and its absorption spectrum are identical to those of benzophenone.

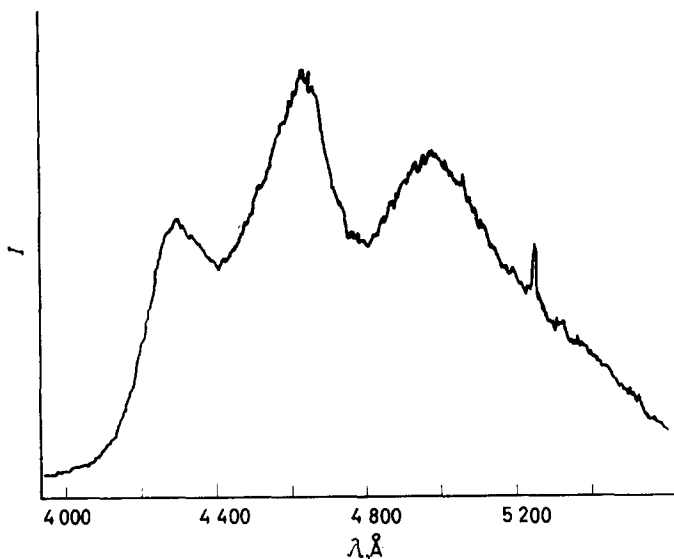


Figure 2—Phosphorescence spectrum of a PVB film irradiated at 77°K with 3650 Å light

(3) Irradiation technique

This has been described previously³. The intensity of the Philips HPK 125 W lamp equipped with a monochromatic filter Iena Hg Mon 365 was determined with the benzophenone–benzhydrol actinometer⁵. Incident intensity on the windows of the irradiation cells was 6×10^{-7} E min⁻¹. The stability of the lamp was controlled with a RCA 935 phototube.

(4) Post-irradiation analysis

The unreacted benzophenone or *p*-propylbenzophenone concentrations were determined by absorption spectroscopy at 3400, 3500 and 3600 Å after dilution of the irradiated solutions. Gel content was estimated by subtracting from the initial polymer quantity the soluble polymer amount recovered after centrifugation of the solutions. The latter can be measured by weighing after freeze-drying or by absorption spectroscopy at 3650 Å. Acetone was analysed by vapour phase chromatography on a CarboWax column at 60°C with a Perkin–Elmer F6 apparatus equipped with a flame ionization detector. The presence of low molecular weight hydrocarbons and carbon monoxide formed on photolysis of *p*-propylbenzophenone was investigated by the same method on a di-2-ethylhexylsebacate column at 30°C using an apparatus fitted with a thermal conductivity cell.

RESULTS

(1) Photolysis of *p*-propylbenzophenone

Photolysis of *p*-propylbenzophenone was studied in isopropanol, in an isopropanol–benzene mixture and in benzene in order to allow a comparison of the results with those obtained for benzophenone on the one hand and

Table 1. Quantum yields for disappearance of carbonyl groups and formation of acetone at 3 650 Å. (Intensity on cell window : 6×10^{-7} E min⁻¹.)

	<i>Product</i>	<i>Solvent</i>	t_{irr}	$\phi(\text{C}=\text{O})$	$\phi(\text{acetone})$
1	Benzophenone 5×10^{-2} M	Isopropanol	8h	1.56	0.86
2	Propylbenzo- phenone 5×10^{-2} M	"	8h	1.66	0.82
3	Propylbenzo- phenone 3.3×10^{-2} M	Benzene + 10^{-1} M isopro- panol	8h	1.24	0.58
4	"	Benzene	1h30	2×10^{-2}	—
5	PVB B 3.36×10^{-2} M	Benzene + 10^{-1} M isopro- panol	8h	—	0.25

for PVB on the other hand. The quantum yields for *p*-propylbenzophenone disappearance and acetone formation are gathered in *Table 1*. The absorption of the carbonyl group was no longer visible in the infra-red spectrum of *p*-propylbenzophenone after 24 h irradiation while new bands appear at 1 035 and 1 500 cm⁻¹ (these are also observed in the infra-red spectrum of benzpinacol). Quantum yield for propane formation is 2×10^{-4} . Carbon monoxide, methane, ethane, ethylene, acetylene and propylene were not detected (quantum yield less than 3.5×10^{-5}).

(2) *Photolysis of PVB in solution*

(a) *Diluted solutions* (0.4 wt per cent)—The specific viscosity change for diluted PVB solutions was studied as a function of irradiation time in pure benzene and in benzene containing various amounts of naphthalene and isopropanol (*Figure 3*). The viscosity decreases faster in benzene-isopropanol mixtures (curve 3) than in pure benzene (curve 1).

Naphthalene inhibits the viscosity decrease process (curves 2 and 4). This inhibition is more effective when the naphthalene concentration is higher (curve 5).

Experiments leading to curve 3 were also performed with a ten times lower intensity, but no initial viscosity increase was observed. The amount of gel after 8 h irradiation never exceeds five per cent. Quantum yields for acetone formation are given in *Table 1*. The same modifications in the infra-red spectrum occur as with *p*-propylbenzophenone.

Table 2. Photolysis of PVB films at 3 650 Å

<i>PVB</i>	<i>Naphthalene</i> wt %	<i>Irradiation time</i> h	% gel
A	—	1	30
A	5	1	0
A	—	2	63
A	—	4	83
B	—	5	50
B	5	5	0

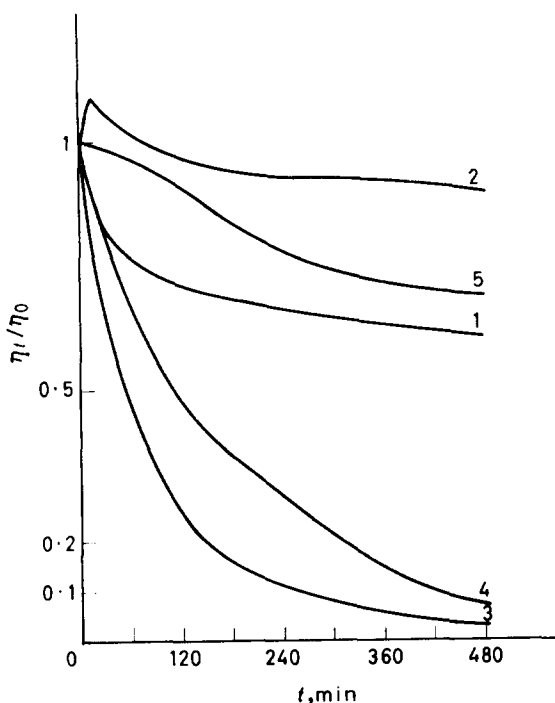


Figure 3— η_t/η_0 for PVB solutions as a function of irradiation time (η_0 denotes specific viscosity before irradiation, η_t is the specific viscosity after t min irradiation). Curve 1 : PVB 2.02×10^{-2} M in benzene; Curve 2 : PVB 2.02×10^{-2} M in benzene+naphthalene 10^{-3} M; Curve 3 : PVB 2.16×10^{-3} M in benzene + isopropanol 10^{-1} M; Curve 4 : PVB 2.16×10^{-2} M in benzene + isopropanol 10^{-1} M+naphthalene 10^{-3} M; Curve 5 : PVB 2.16×10^{-2} M in benzene+isopropanol 10^{-1} M+naphthalene 10^{-2} M. (Polymer concentrations are in moles of monomeric units per litre)

(b) *Concentrated solutions* (between 2.9 and 6 wt per cent)—The gel fraction formed in concentrated PVB solutions in benzene containing 0.1 mole per litre isopropanol is larger than 95 per cent after 8 h irradiation.

(3) *Photolysis of PVB films* (0.01 mm thick)

The results are summarized in *Table 2*. A gel fraction up to 100 per cent is formed. Inhibition by naphthalene was observed.

DISCUSSION

Formation of alcohols or pinacols, disappearance of C=O absorption in the infra-red spectrum and acetone formation in solutions containing isopropanol show clearly that photoreduction of the carbonyl group occurs when PVB is irradiated at 3 650 Å.

Three types of reaction are liable to occur by reaction of the intermediate radicals formed:

(a) Intermolecular recombination leading to an increase of the molecular weight and to the formation of an insoluble gel.

(b) Intramolecular recombination bringing about cyclization (without an increase of the molecular weight) and a decrease of the limiting viscosity number due to a reduction of the hydrodynamic volume of the macromolecule.

(c) Reaction with the hydrogens of the main chain giving rise to scission of the macromolecule and a lowering of the limiting viscosity number.

In dilute solution no appreciable amount of gel is formed and a decrease of the specific viscosity is observed. The first hypothesis is thus excluded. Moreover this viscosity change must be attributed to cyclization rather than rupture of the polymer chain since no breaking of the side chain is observed when *p*-propylbenzophenone is irradiated.

However, with concentrated solutions and solid films the most important mechanism is the intermolecular recombination of the radicals formed by photoreduction since 100 per cent gel can be obtained. Such a concentration effect has already been observed in the radiolysis of polyvinylchloride⁷ and polyvinylalcohol solutions⁸.

Cyclization of PVB in dilute solutions and crosslinking in concentrated solutions or solid films are both inhibited by naphthalene. The photoreduction of benzophenone is also inhibited by naphthalene. This has been demonstrated to be due to a deactivation of the benzophenone $n-\pi^*$ triplet state ($\nu_{0-0} = 24\,250\text{ cm}^{-1}$) by energy transfer to the naphthalene triplet state ($\nu_{0-0} = 21\,250\text{ cm}^{-1}$). Comparison of the absorption and phosphorescence spectra of PVB and benzophenone indicates that the lowest excited state of both compounds is an $n-\pi^*$ triplet corresponding to almost the same energy ($\nu_{0-0} = 23\,200\text{ cm}^{-1}$ for PVB). It must thus be concluded that the photoreduction of PVB also proceeds by a triplet state mechanism.

The specific viscosity decrease due to cyclization is much more important in benzene-isopropanol mixtures than in pure benzene. Isopropanol is thus a much more effective hydrogen donor than the polymer itself. A similar reactivity difference has been observed between isopropanol and toluene: quantum yields for benzophenone disappearance reach values of 2 and 0.38 respectively in these solvents.

The reactivity of the carbonyl group in *p*-propylbenzophenone can be compared with that of the same group in PVB. *Table 1* shows that, in the same conditions, the quantum yield for acetone formation is 0.58 in the first case and 0.25 in the second. Although the mechanism is qualitatively the same, a quantitative difference is thus observed; it is most probably due to the reduced accessibility of the excited carbonyl group inside the macromolecular coil. For the same reason, polymers are also less sensitive to the quenching of metastable states than small molecules⁹.

CONCLUSION

The photochemical behaviour of polymers containing the phenylketone group depends on the presence of a labile hydrogen in γ position relative to the carbonyl group. Therefore irradiation of polyphenylvinylketone at 3 650 Å leads to chain scission with a quantum yield independent of the

presence of isopropanol or naphthalene while in the same conditions PVB is cyclized or crosslinked by a triplet state mechanism.

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