Photoactive polymers containing vanadium: 1. Preparation, characterization and photoreactions

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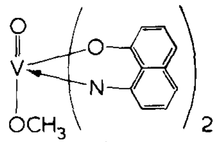
Photoactive polymers have been prepared by reaction of VOQ_2OH (Q = 8-quinolyloxo) with polymers of types A and B carrying pendant hydroxyl groups. Type A was represented by copolymers of methyl methacrylate and 2-hydroxyethyl methacrylate and type B by a copolymer of styrene and *p*-vinylbenzyl alcohol. The final copolymers are designated VA, VB, respectively. The copolymers were characterized by near u.v.–visible spectra. On irradiation ($\lambda = 365$ nm) the vanadium (IV) chelate VOQ_2 is formed; this is indicated by the u.v.–visible spectral changes, and also by e.s.r. spectroscopy. The infra-red spectra of the copolymers VA, VB show important differences, notably the presence of a strong band near 960 cm^{-1} (attributable to V=O stretching vibrations) in the former and its absence from the latter. From this and other evidence it is concluded that the vanadium residues have different structures in the two types of copolymer, viz. $O{=}VQ_2{-}OR$ and $(HO)_2VQ_2{-}OR$ in VA and VB respectively, where R is the remainder of the copolymer molecule. Irradiation ($\lambda = 365$ nm) is considered to bring about scission of V–OR bonds in copolymer VA with formation of a macroalkyloxy radical $\dot{O}R$. This is consistent with spin-trapping experiments with benzylidene nitrone. On the other hand, photolysis of copolymer VB appears to give radicals identical with those from VOQ_2OH which are most probably $\dot{O}H$.

The formation of different types of radical on irradiation of copolymers VA, VB is also indicated by spin-trapping observations with nitrosodurene in benzene solution and also the occurrence of photografting when VA (but not VB) is irradiated in a monomer. The photolysis of VOQ_2OH to which we have referred above may provide a convenient source of hydroxyl radicals in non-aqueous solution.

INTRODUCTION

We have recently studied the photochemistry of some vanadium (V) chelates[1–3] including methoxo-oxobis (8-quinolyloxo) vanadium (V)[3] (I):



(I)

which we shall subsequently abbreviate to VOQ_2OCH_3, Q representing the 8-quinolyloxo ligand. This chelate is a photoinitiator of free radical polymerization by virtue of scission of the $V{-}OCH_3$ bond which occurs on irradiation ($\lambda = 365$ nm) (equation 1). We believe that this mode of photodecomposition is general for chelates of this type which carry alkyloxy groups and is therefore a useful source of 'alkyloxy' radicals $(OR)^{\cdot}$ in non-aqueous solution[4]

$$VOQ_2OR \xrightarrow{h\nu} VOQ_2 + (OR)^{\cdot} \qquad (1)$$

The structure of the radical products is discussed later in this paper and also in a separate publication[4]. The photochemical applications of vanadium (V) chelates are by no means limited to those summarized by equation (1). We have found that many different radical species, e.g. $\dot{O}H$, $\dot{S}H$, $\dot{S}R$, $(C_2H_5)_2NC(=S)\dot{S}$ may be conveniently generated by photolysis of the appropriate chelate and we hope to report on this in the near future.

It occurred to us that a photoactive polymer based on (I) could by synthesized by making R part of a polymer chain; photolysis according to equation (1) should then yield reactive macroradicals which could participate in grafting and crosslinking reactions under suitable conditions. In view of the great current interest attached to photoactive polymers, it seemed that this approach might lead to the development of practically useful materials.

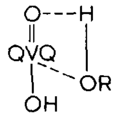
The synthesis and photodecomposition of derivatives of type (I) are clearly of paramount importance in the present project and relevant information on these topics is summarized below.

The first synthesis of (I) was effected by Blair *et al.*[5] who utilized the reaction:

$$VOQ_2OH + ROH \longrightarrow VOQ_2OR + H_2O \qquad (2)$$

These workers mainly studied the lower alcohols (R = CH_3, C_2H_5, i-Pr) and showed that VOQ_2OR may readily be prepared by refluxing VOQ_2OH in the bulk alcohol for two hours. After filtration of the liquid the required product was isolated on cooling to 0°C for 2–3 h and then purified by recrystallization from the alcohol.

Blair *et al.*[5] suggested that in order to achieve a satisfactory preparation the water produced in reaction (2) must be removed by excess alcohol, which acts as a dehydrating agent. In solutions of low alcohol content, VOQ_2OH apparently forms an intermediate complex which, however, is unstable and decomposes into the starting materials on removing the solvent. Pilipenko *et al.*[6] agreed generally with the conclusions of Blair *et al.* and proposed that the intermediate complex has the structure:



(II)

Removal of water from (II), e.g. by excess alcohol, was considered to produce the required ester product VOQ_2OR. Blair *et al.*[5] suggest that the intermediate complex and the ester product have indistinguishable u.v. absorption spectra.

The kinetics of the polymerization of methyl methacrylate photoinitiated by (I) (λ = 365 nm) are consistent with an uncomplicated free-radical polymerization so long as $[(I)] < 4 \times 10^{-5}$ mol l^{-1}, approximately[3]. The rate of initiation is independent of the monomer concentration, so that monomer does not enter into a rate-determining process in initiation. The quantum yield of initiation is 2.26×10^{-3} and it turns out that each molecule of (I) which decomposes yields one initiating radical[3]. Spectroscopic observations (i.r., u.v.–visible, e.s.r.) have shown that on photolysis rupture of the $V{-}OCH_3$ bond leads to the stable vanadium (IV) chelate VOQ_2. The nature of the initiating species is a matter of some interest. Work with (I) labelled with ^{14}C in the methyl group showed that the polymeric products possess the radioactivity expected if initiation occurs solely by the methyloxy radical[3]. Spin-trapping experiments with benzylidene-t-butylamine *N*-oxide as radical scavenger revealed that at low concentrations of scavenger (0.008 mol l^{-1}) the only radical trapped is $\dot{C}H_2OH$ while at higher concentrations (0.35 mol l^{-1}) mixtures of $CH_3\dot{O}$ and $\dot{C}H_2OH$ may be trapped. These results are understandable if $CH_3\dot{O}$ is the primary product of photolysis and rapidly isomerizes to $\dot{C}H_2OH$. Other workers[7] have reported this isomerization in the course of studies on the oxidation of methanol and attributed it to interaction between $CH_3\dot{O}$ and methanol generating $\dot{C}H_2OH$. Clearly this explanation does not apply to the present system; consequently, we believe that the isomerization is characteristic of the alkyloxy radical and is not dependent on reaction with alcohol (cf. Berdnikov *et al.*[8]). It is very probable that oxygen macroradicals obtained from the photoactive polymers discussed below will isomerize rapidly to carbon radicals but this should not interfere with their ability to initiate graft polymerization.

EXPERIMENTAL

An earlier paper[3] describes the preparation (when necessary) and purification of most of the starting materials and also the techniques employed. In addition nitrosodurene was synthesized by the method of Smith and Taylor[9] and 2-hydroxyethyl methacrylate was purified as described in the patent literature[10].

Preparation of polymers containing vanadium

In principle, the photoactive polymers which we wish to study could be prepared either from polymers containing hydroxyl groups or from a monomer in which the methyl of (I) is replaced by a polymerizable group. The latter procedure encounters considerable difficulties since concentrations of V^V chelates exceeding 10^{-3} mol l^{-1} are strong retarders of free-radical polymerization and much higher concentrations are normally required for copolymerization. We have therefore adopted the former method.

Two types of hydroxyl-containing copolymers have been prepared. Type A consisted of copolymers of 2-hydroxyethyl methacrylate (HEMA) with methyl methacrylate (MMA) while type B was a copolymer of *p*-vinylbenzyl alcohol and styrene the synthesis of which has already been reported[11].

Copolymers of HEMA and MMA were prepared at 60°C with azobisisobutyronitrile (5×10^{-3} mol l^{-1}) as initiator, conversions being limited to 2%. Volume fractions of HEMA in the feed were 2, 5, 10%. *Table 1* shows the mole fractions and the mean sequence lengths of the monomer units in the copolymers; these were calculated from the feed compositions and the reactivity ratios: r_1 (HEMA) = 1.267, r_2 = 0.141, which were determined by a method which will be described in a forthcoming publication[12]. The copolymers were reprecipitated four times from benzene solution into methanol and dried at 80°C overnight in vacuum.

Copolymers containing vanadium chelate residues were prepared from the above copolymers according to reaction (2). The copolymers A_1, A_2 and A_3 were refluxed in dry benzene in the presence of hydroxo-oxobis-8-quinolyloxo vanadium (V) (VOQ_2OH) for suitable periods from 15 to 90 min. The resulting red solutions were poured into excess dry cyclohexane and the precipitated red copolymers (VA_1, VA_2 and VA_3) were purified by reprecipitation into cyclohexane. They were dried in vacuum at room temperature (~2h). Copolymer VA_1 which was used in the experiments described below was prepared with a reflux time of 60 min. The vanadium content of this copolymer was determined by u.v. absorption on the assumption that the extinction coefficient of the chelate residues is 4910 mol l^{-1} cm^{-1} at λ = 365 nm, i.e. the same as for (I). This method gave 2921 ppm V. From the data in *Table 1* it follows that in a polymer chain with $\bar{M}_n = 7 \times 10^5$ (the approximate number-average molecular weight of A_1) there are on average 40 V atoms. The average number of OH groups initially in the chain is about 1700, hence approximately 2% of these react according to reaction (2) during refluxing.

Copolymer B contained a mole fraction of OH close to 0.02. The corresponding 'red' copolymer (VB) was prepared as described above, although a longer period of refluxing (normally 2 h) was required.

Table 1

Copolymer	Feed composition concentrations (mol l^{-1})	Copolymer composition (mole fractions)		Mean sequence lengths in copolymer	
	[HEMA]/[MMA]	HEMA	MMA	HEMA	MMA
A_1	0.0973	0.314	0.686	1.12	2.45
A_2	0.0461	0.207	0.793	1.06	4.06
A_3	0.0179	0.103	0.897	1.02	8.88

RESULTS AND DISCUSSION

Characterization of vanadium-containing copolymers

U.v.–visible spectroscopy. The near u.v.–visible spec-

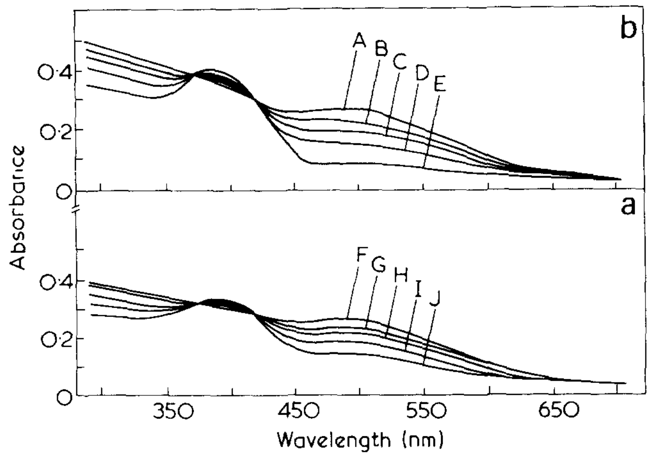


Figure 1 Spectral changes occurring on irradiation (λ = 365 nm) at 25°C. (a) Copolymer VA$_1$ in MMA solution. Times of irradiation (min): A, 0; B, 2; C, 5; D, 10; E, 20; (b) VOQ$_2$OMe in bulk methanol. Times of irradiation (min): F, 0; G, 8; H, 30; I, 92; J, 174. Polymer concentration 0.625 g l^{-1}

trum of copolymer VA$_1$ in methyl methacylate solution is presented in *Figure 1a;* while it is similar to that of VOQ$_2$-OCH$_3$ in MMA[3] there are some differences, the most evident being a relatively lower extinction coefficient for VA$_1$ in the visible region. The significance of this is discussed in Part 2. Similar spectra are obtained from benzene and ethyl acetate solutions. On irradiation with light of λ = 365 nm the spectral changes shown in *Figure 1a* occur. The similarity in behaviour between VA$_1$ and (I) is again apparent, notably the existence of two isosbestic points. The band near 400 nm is characteristic of V^{IV} derivatives and arises from d–d transitions[13].

In methanol solution the spectral changes during photolysis of (I) are somewhat different from those in MMA (compare *Figure 1b* with *Figure 3* of ref 3). The d–d transition near 400 nm is sensitive to the nature of the medium; for example, it is situated at 400 nm and 390 nm in MMA and methanol, respectively. It is important to notice that this band occurs at 390 nm in the spectrum of copolymer VA$_1$ in MMA solution (*Figure 1a*); indeed the final spectra shown in *Figures 1a* and *1b* are essentially identical. It has been proposed by Guzy *et al.*[14] that V^{IV} chelates such as VO(acac)$_2$ form hydrogen bonds of the type shown below with alcohols;

O . . . HOR
||
V(acac)$_2$

these workers also reported that in the presence of methanol the 400 nm band appears at shorter wavelengths. We therefore conclude that the product VOQ$_2$ from the photolysis of (I) in methanol is hydrogen bonded to the alcohol. Further, VOQ$_2$ formed by photodecomposition of copolymer VA$_1$ in MMA solution is also hydrogen bonded, the hydroxyl groups in this case being those attached to the polymer chain.

E.s.r. spectroscopy of products. Copolymers of types VA and VB containing V^V derivatives are diamagentic. After irradiation of the copolymers in methyl methacrylate or in benzene, the solutions give an e.s.r. spectrum characteristic of V^{IV} species. This is eight-line spectrum which has previously been recorded for the products of photoreduction of VO(acac)$_2$Cl[1] its dimethyl sulphoxide adduct[2] and VOQ$_2$-OMe[3].

The observations we have described support the view that irradiation brings about the photoreduction of V^V in the VA copolymers to V^{IV}, probably with rupture of the V–OR bond as in the case of (i) (equation 1). The photodecomposition of copolymer VB is discussed below.

I.r. spectra. Figure 2 presents a comparison of the i.r. spectra in the region between 800 and 1200 cm^{-1} of copolymers A$_1$ and VA$_1$. The band near 960 cm^{-1} is relatively much stronger in VA$_1$ and arises in this case mainly from V=O stretching vibrations (as in VOQ$_2$OR derivatives in general[5,6]). The spectrum of A$_1$ has a weak band near this frequency. Bands at 1106 and 1320 cm^{-1} (not shown in *Figure 2*) are found in the spectrum of copolymers VA$_1$

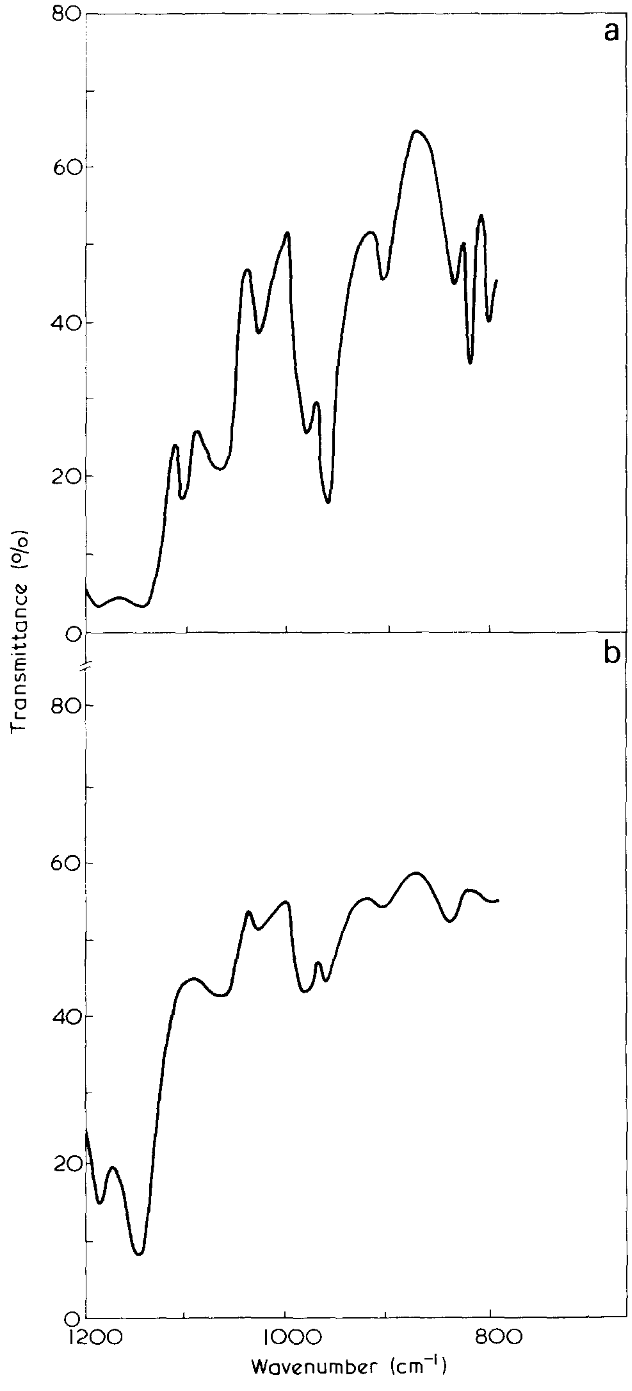
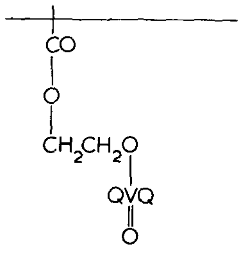


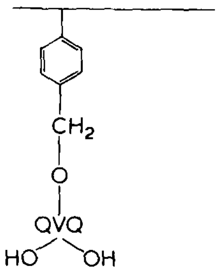
Figure 2 Infra-red spectra of copolymers (a) VA$_1$ and (b) A$_1$ (cast from benzene solutions on to NaCl plates)

only and are attributable[5] to C–O vibrations in the ligand Q.

By contrast, the spectrum of copolymer (VB) in *Figure 3* has no significant band at 960 cm^{-1} other than the weak absorption in copolymer B although the bands at 1106 and 1320 cm^{-1} are present, as with VA_1. It seems clear, therefore, that the vanadium residues have different structures in the two types of copolymer; we believe these correspond to (III) and (IV):



(III)
In copolymers VA

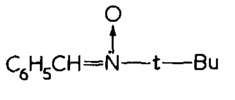


(IV)
In copolymer VB

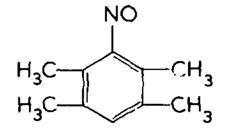
As already mentioned, Blair *et al.*[5] and Pilipenko *et al.*[6] have suggested that reaction between VOQ_2OH and an alcohol yields an intermediate complex (e.g. II) under conditions of low alcohol concentration. The i.r. spectrum favours the seven-coordinate structure (IV) rather than (II) for the vanadium residues in VB. The data in *Table 1* and the OH content given for copolymer B indicate that the three A copolymers contain much higher proportions of OH groups than B, so that the failure of the latter to give the completely esterified structure is understandable.

Nature of radicals arising in photolysis: spin-trapping experiments

Most of the work has been carried out with (V) as spin trap:

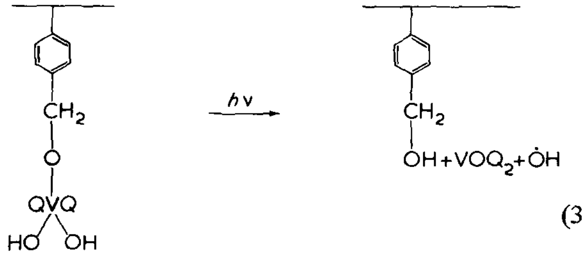


(V)



(VI)

Table 2 shows the hyperfine splitting constants a_N and $a_{\beta H}$ in the e.s.r. spectra obtained after irradiation of different vanadium derivatives in benzene solution in the presence of the spin-trap (10^{-2} mol l^{-1}). All spectra referred to in the table were of the 'triplet of doublets' type. As appears from *Table 2*, the e.s.r. spectra from copolymer (VB) and VOQ_2OH are identical and we propose that they arise from $\dot{O}H$ radicals generated photolytically. In agreement with this, we have obtained u.v. evidence that photolysis of VOQ_2OH yields $V^{IV}OQ_2$. Since the u.v. spectral evidence establishes the formation of VOQ_2 in the photolysis of copolymer VB, the photolytic reaction appears to be:



(3)

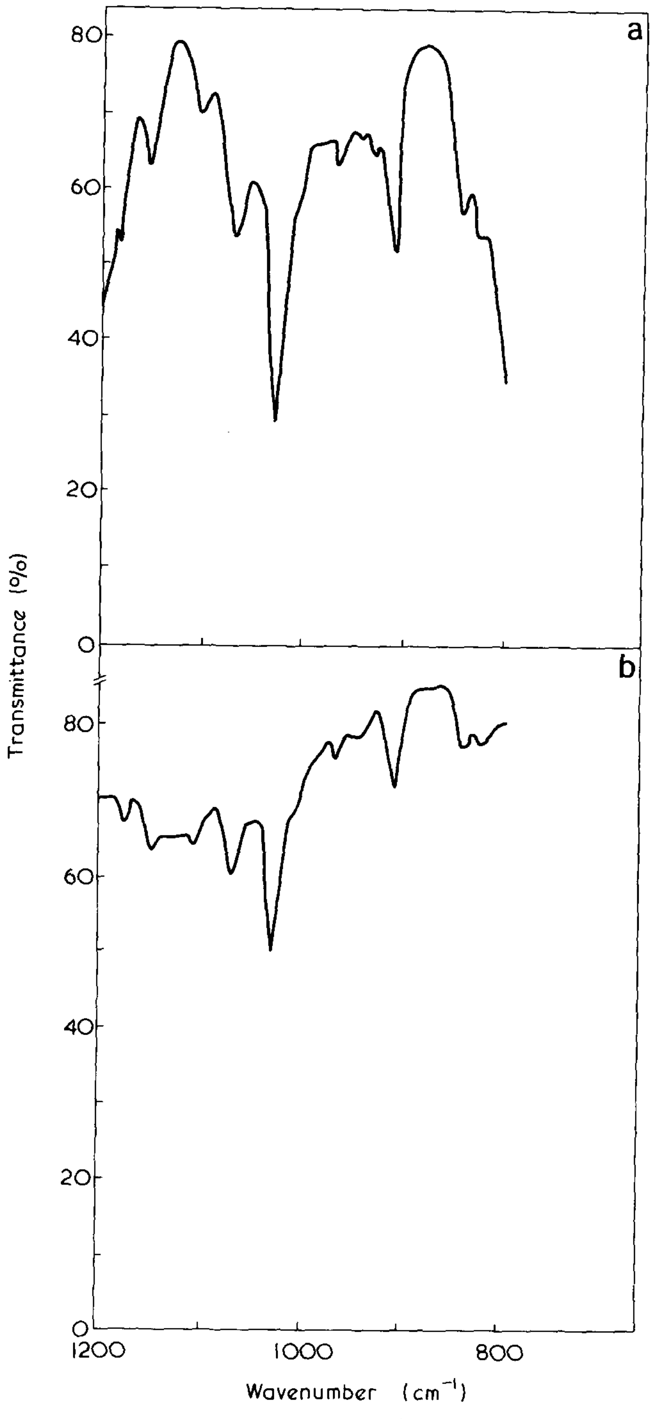


Figure 3 Infra-red spectra of copolymer (a) VB and (b) B (cast from benzene solution on to NaCl plate)

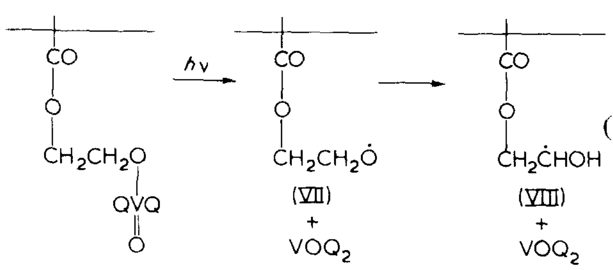
Table 2 Spin-trapping by $PhCH{=}\overset{O}{\overset{\uparrow}{N}}\text{-t-Bu}$ (10^{-2} mol l^{-1}) at 25°C

Compound photolysed (λ = 365 nm)	a_N(G)	$a_{\beta H}$(G)
Copolymer VA_1	14.88	2.17
Copolymer VB	15.14	2.23
VOQ_2OH	15.14	2.23
$VOQ_2OCH_2C_6H_5$	14.65	3.37

The chelate $VOQ_2OCH_2C_6H_5$ was prepared from bulk benzyl alcohol and VOQ_2OH (Blair *et al.*[5]), a process similar to that employed in the synthesis of copolymer VB although in the latter case benzene solutions were used. According to *Table 2*, photolysis of $VOQ_2OCH_2C_6H_5$ produces a species different from $\dot{O}H$ which we believe to be the isomerized benzyloxy radical $C_6H_5\dot{C}HOH$. At a higher concentration (0.2 mol l^{-1}) of spin trap a more complex e.s.r. spectrum was observed from which we found $a_N = 13.68$ G and $a_{\beta H} = 2.31$ G for the major component. The latter therefore is likely to be $C_6H_5CH_2\dot{O}$, which is trapped before isomerization can occur by high concentrations of (V). Values of a are sensitive to the electron-density on the carbon atom carrying the unpaired spin; the high value of $a_{\beta H}$ for $C_6H_5\dot{C}HOH$ compared to $C_6H_5CH_2\dot{O}$ results from electron donation by the phenyl group.

Polymerization experiments were carried out to investigate the nature of the radical formed by photolysis of $VOQ_2OCH_2C_6H_5$. The latter, prepared from benzyl alcohol with its methylene groups labelled with ^{14}C, was used to photoinitiate the polymerization of methyl methacrylate at 25°C. The polymer was purified by several reprecipitations from benzene into methanol and its activity and molecular weight were determined. On average each molecule contained 1.20 $C_6H_5CH_2O$ (or C_6H_5CHOH) groups, a value very close to that expected (1.21) if initiation occurs exclusively by species of the type labelled (the ratio of combination to disproportionation in the termination reaction in the polymerization of MMA at 25°C being taken as 0.52[15]). Initiation by $\dot{O}H$ would clearly give polymers without any activity. These experiments show that the structure of the vanadium group in (VB) is not equivalent to $VOQ_2OCH_2C_6H_5$ and so support the views of Blair *et al.*[5] that excess of alcohol is necessary for a successful synthesis according to reaction (2).

On the other hand, *Table 2* reveals that the radical formed by photolysis of copolymer VA is not $\dot{O}H$ but is presumably the macro-alkyloxy radical (VII) or its isomer (VIII):



(4)

In fact, isomerization of the radical is likely to be complete, since a higher concentration of (V) (0.3 mol l^{-1}) produces a more complicated spectrum (no longer a triplet of doublets), closely resembling that obtained from photolysis of VOQ_2OCH_3 under similar conditions[3]. In the case of copolymer VB, increase in the concentration of (V) is without effect on the spectrum.

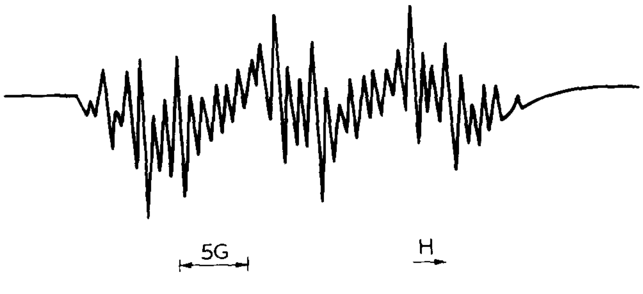


Figure 4 E.s.r. spectra obtained after photolysis (λ = 365 nm, 15 min, 25°C) of copolymer VB (0.6 g l^{-1}) in benzene solution in the presence of nitrosodurene (10^{-3} mol l^{-1}).

When copolymer VB is photolysed in benzene solution in the presence of nitrosodurene (VI) (10^{-3} mol l^{-1}) a 36-line e.s.r. spectrum (*Figure 4*) may be obtained. This must arise from the trapping of a radical derived from the interaction of $\dot{O}H$ and benzene. The splittings agree well with those reported by Terabe *et al.*[16] for the adduct of $C_6H_5\cdot$ and (VI), suggesting the occurrence of hydrogen abstraction from benzene by $\dot{O}H$. However, there is evidence that $\dot{O}H$ interacts with benzene partly by addition[17] so that it is possible that the signal we observe is derived in part from trapped hydroxycyclohexadienyl radicals. These findings are consistent with the postulated photolysis of copolymer VB (equation 3). Similarly, when toluene is the solvent, a well-resolved spectrum indicating formation of the benzyl radical is developed with $a_N = 13.63$ G, $a_{\beta H} = 7.88$ G (compare $a_N = 13.61$ G, $a_{\beta H} = 7.93$ G from ref 16). Identical results follow from irradiation of VOQ_2OH under similar conditions. No spectra can be observed after photolysis of copolymer VA_1 in the presence of (VI). It is known that alkyloxy radicals are not readily trapped by (VI)[16]. Moreover, isomerization probably occurs before the macroalkyloxy radical from VA_1 can attack benzene and the resulting carbon radical would be much less active in hydrogen abstraction.

Photografting

Irradiation of copolymers VA_1, VA_2 and VA_3 in methyl methacrylate solution gave rise to extensive gelation, arising from grafting and crosslinking through the macroradicals produced by reaction (4). By contrast, copolymers of type VB gave only homopolymers of methyl methacrylate without gelation. These results are consistent with the different mechanisms of photolysis in equations (4) and (3).

The reactions described provide a new method of photografting on to polymers carrying hydroxyl groups. In this connection two further points may be noted. First, homopolymerization does not accompany grafting because the vanadium (IV) product VOQ_2 is incapable of initiating and secondly, we find that excess vanadium remaining after reaction may be removed by treatment with methanol, which replaces the vanadium residues by hydroxyl:

$$VOQ_2OR + CH_3OH \longrightarrow VOQ_2OCH_3 + ROH \quad (5)$$

This reaction occurs readily when the solid red copolymers are suspended in methanol at ambient temperature in the dark.

REFERENCES

1 Aliwi, S. M. and Bamford, C. H. *JCS Faraday Trans. I* 1974, **70**, 2092
2 Aliwi, S. M. and Bamford, C. H. *JCS Faraday Trans. I* 1975, **71**, 52
3 Aliwi, S. M. and Bamford C. H. *JCS Faraday Trans. I* 1975, **71**, 1733
4 Aliwi, S. M. and Bamford, C. H. *JCS Faraday Trans I* in press
5 Blair, A. J., Pantony, D. A. and Minkoff, G. J. *J. Inorg. Nucl. Chem.* 1958, **5**, 316
6 Pilipenko, A. T., Shevchenko, L. L. and Zynzya, L. A. *Russian J. Inorg. Chem.* 1973, **18**, 66
7 Ledwith, A., Russell, P. J. and Sutcliffe, L. H. *Proc. R. Soc. (A)* 1973, **322**, 151
8 Berdnikov, N. M., Bazhin, U. K., Fedorov, V. K. and Polyakov, O. V. *Kinet. Catal.* 1972, **13**, 986

9 Smith, L. I. and Taylor, F. L. *J. Am. Chem. Soc.* 1935, **57**, 2370, 2460
10 Stoy, V., Shtol, M., Vodnansky, J. and Kliment, K. Ger. Pat. OLS 2 105 126 (1971); Hersley, L. H. and Sheetz, D. P. U.S. Pat. 3 162 677 (1964)
11 Bamford, C. H. and Lindsay, H. *Polymer* 1973, **14**, 330
12 Aliwi, S. M. and Bamford, C. H. to be published
13 Selbin, J. *Chem. Rev.*, 1965, **65**, 153
14 Guzy, C. M., Raynor, J. B. and Symons, M. C. R. *J. Chem. Soc.* (A), 1969, p 2791
15 Bamford, C. H., Dyson, R. W. and Eastmond, G. C. *Polymer* 1969, **10**, 885
16 Terabe, S., Kuruma, K. and Konaka, R. *Perkin Trans. II* 1973, p 1252
17 Hansen, D. A., Atkinson, R. and Pitts, J. N. *J. Phys. Chem.* 1975, **79**, 1763