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An ESR Study of the UV Photolysis of Styrene and Maleic Anhydride at 90 K

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ABSTRACT

Free radicals produced in styrene and maleic anhydride mixtures and in solutions in acetone and chloroform by UV photolysis at 90 K have been studied by electron spin resonance and changes observed on warming. A doublet spectrum observed in all systems containing maleic anhydride has been assigned to the radical formed by H addition to a carbonyl group in the monomer, and not to the corresponding radical on maleic anhydride units in the copolymer or to the maleic anhydride propagating radical. Interpretations of copolymerization mechanisms based on radicals produced in frozen comonomers in bulk or in solution by photolysis or radiolysis must therefore be viewed with caution.

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INTRODUCTION

Information on the mechanisms of copolymerizations may be obtained by studying the electron spin resonance (ESR) spectra of the propagating chain radicals. However, the steady-rate concentrations of these radicals in the liquid state are usually too low to observe, and a variety of techniques have been used to increase their concentration. Relative rates of some propagation reactions [1-3] have been obtained by flow ESR. Spin traps have been used in some copolymerizations [4, 5], including maleic anhydride and styrene, but 1) only initial monomer radicals may be trapped, 2) the spin trap may not be equally reactive with all radicals [6], and 3) identification of the trapped radical is difficult. Monomers have been added to precipitated polymer radicals [7], but the relative amounts of radicals from different monomers will be controlled by their rates of diffusion.

An alternative to these methods for obtaining high radical concentrations at normal polymerization temperatures is to produce stabilized radicals by UV or γ-irradiation at low temperatures in the solid state. The conversion from initial to propagating radicals can be observed on warming [8-14]. The presence of only one propagating radical up to T_g [10] has been taken as evidence for propagation solely by addition of the comonomer complex, e.g.,

$$\sim M_1\cdot + \overline{M_2M_1} \longrightarrow \sim M_1M_2M_1\cdot$$

Barton et al. [15], in an ESR investigation of the UV photolysis at 77 K of maleic anhydride-styrene mixtures in acetone and chloroform, could not identify propagating radicals of either monomer. A doublet with hyperfine splitting (hfs) ≈ 1.1 mT was attributed to the radical resulting from H atom addition to a carbonyl group in a maleic anhydride unit in the copolymer molecule. This is in disagreement with the assignment by Smirnov, Golubev, Stoyachenko, and co-workers [8-10] of a similar doublet to the maleic anhydride propagating radical. However, radicals corresponding to propagating species have been identified for maleic anhydride by flow ESR [3, 16] and at low temperatures in a glassy matrix [17] with hfs ≈ 2.0 mT for α-H and 3.4 mT for β-H.

The copolymerization of styrene with maleic anhydride is considered to deviate from normal terminal model behavior, and penultimate effects [18, 19] or participation of comonomer complexes [20-22] have been proposed to explain the copolymer compositions and the initial copolymerization rates.

In this paper we report an investigation of the ESR spectra of styrene and maleic anhydride in bulk and in chloroform and acetone solution following UV photolysis at 90 K in order to clarify the identity of the radicals, and their behavior on warming.

EXPERIMENTAL

Styrene was distilled at 333 K in nitrogen at 5 kPa. Maleic anhydride (AR) was recrystallized twice from chloroform (mp 325.8 K) [21]. Acetone and chloroform were fractionally distilled.

The solvents were deoxygenated with nitrogen for 1 h. Solutions of monomer (1 mol/dm^3) were further deoxygenated, freeze-thaw degassed, and sealed in Spectrosil, high-purity, quartz ESR tubes.

A 1000-W, high-pressure Hg-Xe lamp was focused on the center of the cavity, and filters were used to absorb heat and wavelengths <250 nm.

The ESR spectra were recorded with a Bruker ER200D spectrometer using a variable temperature cavity. The samples were warmed after photolysis in steps of 10 or 20 K and the spectrum obtained after stabilization of the temperature (~200 s).

RESULTS

Acetone Solvent

Photolysis of acetone at 90 K gave the spectrum shown in Fig. 1(A) comprising a quartet with hyperfine splitting (hfs) of 2.2 mT assigned to the methyl radical (I), a singlet attributed to the acetyl radical (II), and a triplet (hfs = 1.95 mT) assigned to the acetonyl radical (III), formed by H atom abstraction. These radicals have been reported with similar ESR spectra in the photolysis of pure liquid acetone [23] and in acetyl chloride-sodium layers condensed on a cold finger at 77 K [24]. Photolysis at 140 K gave a different spectrum comprising mainly acetyl radicals (II) and a septet (hfs = 1.96 mT) attributed to the radical formed by H atom addition to the carbonyl oxygen of acetone (IV) [23]. No methyl radicals were observed at 140 K.

$\dot{C}H_3$	$CH_3\dot{C}O$	$CH_3CO\dot{C}H_2$	$(CH_3)_2\dot{C}OH$
I	II	III	IV

The spectrum from acetone photolyzed at 77 K changed only slightly on warming to 90 K. Methyl radicals decayed rapidly at 90 K and disappeared entirely on warming to 110 K. Acetyl and acetonyl radicals were stable on warming to 140 K, but above this temperature they decayed steadily up to the melting point (178 K). Further work on the kinetics of free radical formation and decay in photolyzed acetone is reported in a separate communication [25].

Photolysis of a frozen solution of styrene (S) in acetone (1 mol/dm^3) at 90 K gave a similar spectrum to that observed for pure acetone, ex-

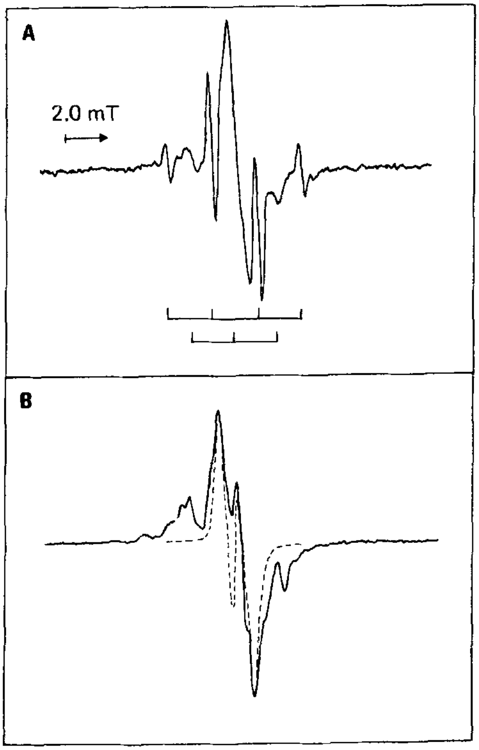


FIG. 1. ESR spectra observed at 90 K following UV photolysis: (A) acetone, (B) maleic anhydride in acetone (1 mol/dm^3). The dashed line shows the simulated doublet for the maleic anhydride radical (hfs 1.0 mT; linewidth 0.75 mT).

cept that the proportion of methyl radicals was increased. No component attributable to radicals from styrene was observed. Apparently styrene increases the stability of methyl radicals or enhances the decomposition of acetyl radicals to methyl radicals.

Photolysis of maleic anhydride (MAn) in acetone (1 mol/dm^3) at 90 K gave a spectrum (Fig. 1B) comprising a doublet with hfs of 1.0 mT and various solvent radicals in smaller amounts, the most important being the singlet of the acetyl radical (II). The proportions of solvent radicals varied in different samples, but the doublet was always predominant. On warming the photolyzed sample, little change was observed below 120 K. Above 140 K the doublet decreased more rapidly than the singlet of the acetyl radical, which was the only species remaining above 160 K. There was no evidence for the formation of any new radicals.

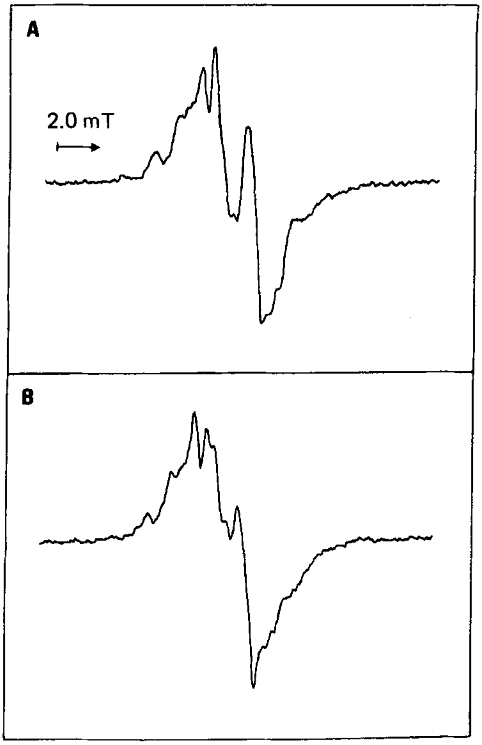


FIG. 2. ESR spectra observed at 90 K following UV photolysis: (A) chloroform, (B) maleic anhydride (1 mol/dm^3) in chloroform.

The photolysis of a mixture of styrene and maleic anhydride in acetone gave a similar spectrum to that of maleic anhydride in acetone, but with a much higher radical concentration. The effect of warming the sample was also similar.

Chloroform Solvent

The ESR spectrum observed after photolysis of $CHCl_3$ at 90 K (Fig. 2A) comprised a broad, asymmetric doublet with hfs ≈ 1.7 mT attributable to the dichloromethyl radical (V) [26]. Hyperfine interaction with the two isotopes of chlorine and the presence of other radical species contributed to the broad shape of the spectrum.

$Cl_2\dot{C}H$

V

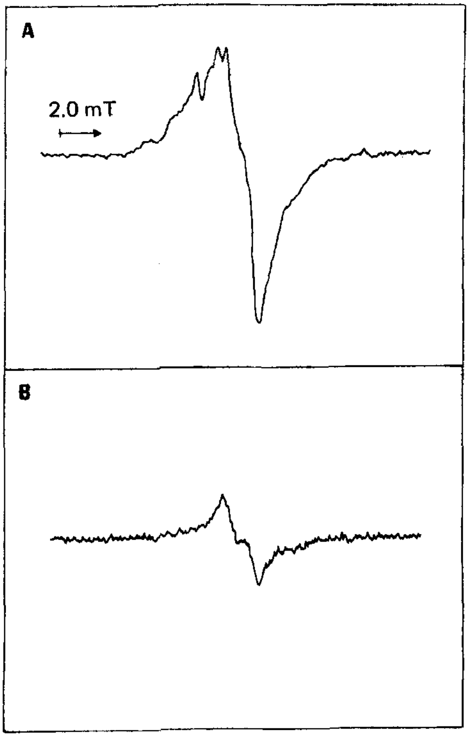


FIG. 3. ESR spectra observed following UV photolysis at 90 K of maleic anhydride (1 mol/dm^3) and styrene (1 mol/dm^3) in chloroform: (A) observed at 90 K, (B) observed at 160 K.

The photolysis of styrene in $CHCl_3$ gave a spectrum similar to that from the pure solvent, but with an additional broad component attributed to a radical from styrene. Photolysis of MAn in $CHCl_3$ gave mainly a spectrum due to the solvent, but also a doublet, similar to that obtained from MAn in acetone (Fig. 2B).

The solvent radicals and the MAn doublet were observed on photolysis of a mixture of S and MAn in $CHCl_3$ (Fig. 3A). The presence of the doublet signal was confirmed by warming the sample. Little change was observed up to 130 K, but above this temperature the total intensity decayed rapidly. The solvent radicals decayed preferentially, leaving a doublet signal with hfs ≈ 1.0 mT at 160 K (Fig. 3B). Again, no new radicals were observed on warming.

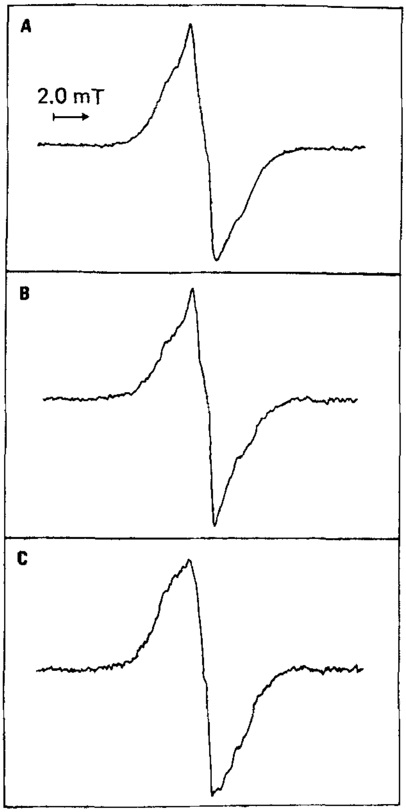


FIG. 4. ESR spectra: (A) observed at 90 K following UV photolysis of a mixture of maleic anhydride and styrene (5:95), (B) simulation of the spectrum for maleic anhydride radical added to styrene spectrum, (C) from photolysis of styrene at 90 K.

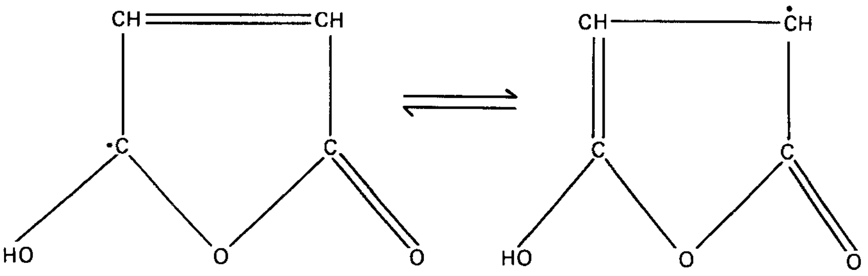
Absence of Solvent

Photolysis of a mixture of maleic anhydride and styrene (5:95) at 90 K in the absence of solvent gave a broad spectrum with a narrow, superimposed doublet (Fig. 4A). The spectrum could be simulated (Fig. 4B) using a doublet of hfs = 1.0 mT (5%) added to the broad spectrum observed by photolysis of pure styrene at 90 K (Fig. 4C) (95%). On warming, the relative proportions of the two components remained constant as the total intensity decreased. The radicals disappeared at 240 K.

DISCUSSION

Photolysis at 90 K is well below any solid-state transitions in the matrix, and polymerization should be suppressed. Both monomers and both solvents would absorb the UV radiation ($\lambda > 250$ nm). Styrene and maleic anhydride form a strong comonomer complex ($K = 0.25$ dm^3/mol at 303 K [20, 21]) and they individually complex with both solvents ($K = 0.05$-0.53 dm^3/mol at 303-313 K [20, 21]). These complexes would be expected to remain when the solutions are cooled to 90 K and to be chromophores for absorption of radiation.

From the photolysis of the comonomers in bulk or in the presence of either solvent, only radical species associated with maleic anhydride could be identified. The doublet of hfs ≈ 1.0 mT observed in all samples containing MAn is assigned to radical VI resulting from H atom addition to a carbonyl group of the anhydride. This radical has been identified by Zott and Heusinger [16] during the photolysis of MAn in dimethylformamide at 123 K using flow ESR and by Fukaya et al. [17] after γ-irradiation of frozen solutions of MAn in 2-methyltetrahydrofuran (MTHF) at 98 K. The large hfs (1.0 mT) of the γ-H can be explained in terms of the resonance structures shown below. The smaller β-H and hydroxy-H splittings are not observed because of the large linewidths associated with the spectra.

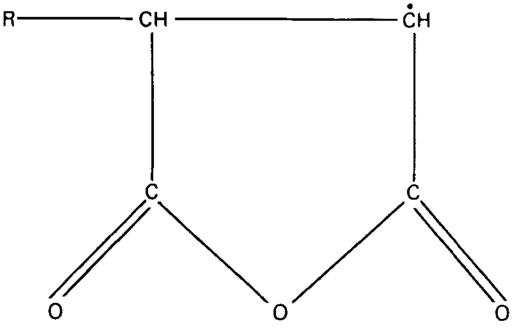


VI

The broad spectrum obtained on photolysis of S or MAn/S in the absence of solvent did not contain observable fine structure so that definite identification was not possible. However, the total width of the spectrum is consistent with radicals formed by addition to the vinyl bond [18].

The MAn anion radical and radicals resulting from addition to the MAn double bond have also been reported, together with radical VI, after radiolysis of frozen solutions of MAn in MTFH [17] and in flow ESR experiments [3, 16]. A contribution from the anion radical (triplet, hfs ≈ 0.65 mT) cannot be ruled out in the present work because of the large linewidths in the spectra. However, the spectra can be satisfactorily explained in all cases by invoking only a doublet due to the MAn radical. This is shown by the simulation superimposed on Fig. 1(B). The MAn anion radical was only observed in flow experiments at relatively low concentrations of MAn [16], and in frozen solutions it was observed to decay at 98 K [17].

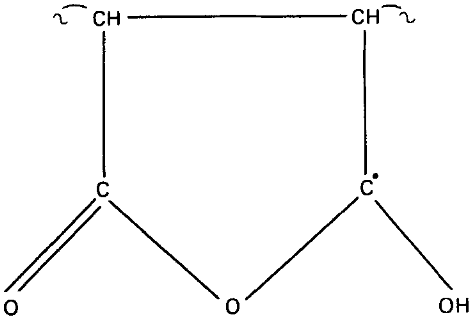
The ESR spectra of radicals resulting from addition to the double bond of MAn, including the propagating radical (VII),



VII

would have α-H hfs of ≈2.0 mT and β-H splittings of ≈3.4 mT regardless of the nature of the adding radical R [3, 16, 17] and would be readily identifiable by components in the wings of the spectrum. No such radicals were observed in the present study after photolysis at 90 K or on subsequent warming of the samples until the signals disappeared.

The spectra obtained in this work are generally better resolved than those of Barton et al. [15] and allow positive identification of radicals in cases where the interpretation was previously difficult. In the system MAn | S | $CHCl_3$, Barton et al. attributed a doublet of hfs ≈ 1.1 mT to a radical formed by H atom addition to a carbonyl oxygen of a MAn residue in the copolymer (VIII).



VIII

We have assigned this doublet to the MAn monomer radical (VI). We have observed that the presence of copolymer enhances the doublet in mixtures containing MAn. However, a high yield of the doublet species is still observed in the absence of polymer, and photolysis of copolymer in solvent in the absence of MAn failed to produce any radicals other than from the solvent.

Stoyachenko et al. [8], Golubev et al. [9], and Smirnov et al. [10] observed a doublet of hfs ≈ 1.1 mT following γ-irradiation at 77 K of mixtures of maleic anhydride with dimethylbutadiene (DMBD), phenyl vinyl ether (PVE), and butyl vinyl ether (BVE). The concentration of the doublet decreased on warming the samples, but sufficient concentrations of the species remained above the thawing temperature of these systems for their spectra to be observed. They assigned this doublet to the propagating radical of MAn (VII). This assignment conflicts with the reported large splittings of α-H and β-H atoms following radical addition to the double bond of MAn both in flow ESR [3, 16] and frozen systems [17].

It is likely that the radical observed by these workers is the monomer radical VI and not the propagating radical. The doublet observed in the present work displayed similar behavior on warming, and polymer was also found after melting. Therefore, previous conclusions [8-10] in favor of free monomer addition in MAn-DMBD and MAn-PVE systems, and propagation solely by complex addition in the MAn-BVE system, are doubtful, since they were based on the interpretation of the doublet as the MAn propagating radical.

While the observation of propagating radicals can be used to study copolymerization, the absence of propagating radicals of either comonomer, especially below the glass transition temperature of the system, cannot be considered as reliable evidence concerning the mechanism of copolymerization. The stability of radicals formed in frozen systems is known to be very dependent on the nature of the matrix, and the rate of heating will often determine whether trapped radicals are involved in propagation or react in other ways to form nonradical species [27].

Although MAn radicals were observed in all the solutions and bulk mixtures containing MAn, they were formed in greatest concentration in solutions in acetone. Styrene radicals, on the other hand, were predominant in the bulk system and were not observed in acetone as solvent. This marked change in the relative proportions of S and MAn radicals shows the importance of the solvent in this system. Measurements of copolymer compositions and copolymerization rates have also shown significant solvent effects [20-22]. Although comonomer and solvent-monomer complexes are present in appreciable concentrations and can be expected to affect the reactivities of the monomers, complexation of radicals by solvent or monomer may also be an important factor influencing radical stability and reactivity both in polymerization at high temperatures [28] and following irradiation at low temperatures [11].

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