

ELECTRON SPIN RESONANCE SPECTRA OF POLYMERS DURING FLUORINATION

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SUMMARY

ESR spectra characteristic of peroxy radicals appeared rapidly in all of eleven hydrogen-containing polymers examined when treated with dilute fluorine. These radicals presumably result from the reaction of hydrocarbon and fluorocarbon radicals, existing at undetectably low steady-state concentrations, with the oxygen impurity content of commercial fluorine. In poly(vinylidene fluoride) films of thickness 11 and 58 μm the radical contents were nearly proportional to surface area rather than volume, in agreement with earlier reports of a shallow depth of penetration. Some polymers exhibited also or exclusively a broad spectral component, varying in character with the polymer; examples are polystyrene, polyethylene, poly(vinyl chloride), poly(vinylidene chloride), polyoctafluoropentadiene, polyhexafluoropropene, and a fluorinated graphite. The broad spectral component did not react with ordinary radical scavengers such as propylene and oxygen, and is probably not due to a fluorocarbon radical but to unknown transition metal fluorides.

INTRODUCTION

It is usually accepted that the reaction of fluorine gas with hydrocarbons is a free radical chain reaction [1-3]. Some reinvestigation appears desirable in connection with the reported smooth and complete fluorination of hydrocarbon polymers [4-8], since crosslinking and scission would be anticipated as important side reactions of a radical chain process. A preliminary note disclosed the detection of radicals by electron spin resonance (ESR) spectroscopy in polyethylene and polystyrene

treated with dilute fluorine at room temperature [9]. Extensions of this work resulted in the attainment of useful degrees of crosslinking by exposing certain fluorine-bearing copolymers to the action of dilute fluorine gas [10,11]. Others have reported the formation of free radicals upon treating olefinic monomers and unsaturated polymers [12,13] with fluorine. The purpose of the present account is to furnish further details on the ESR spectra of the radicals. The formation of peroxy radicals was found to be very widespread when polymers were contacted with dilute commercial fluorine containing the usual oxygen impurity. However, the earlier tentative identification of a broad spectral component as due to fluorocarbon free radicals now appears unlikely.

EXPERIMENTAL

Fluorine diluted with helium was led through a copper tubing system over a 0.1 - 0.3 g sample of polymer supported in a tube of polytetrafluoroethylene or fused silica, mounted in the cavity of an electron spin resonance spectrometer. Provision was made for nitrogen flushing, for additional dilution of the initially 2% or 5% fluorine with nitrogen, for controlled injection of other gases during or after fluorination, and for heating the cavity and contents by an external hot air blast to temperatures up to 55°C. Overall weight changes were measured. In a few instances, samples after fluorination were removed to quartz tubes and heated in vacuum or air at temperatures ranging up to 130°C to observe further changes in electron spin resonance spectra. Elemental analyses and neutron activation analyses were also done on selected specimens.

RESULTS

In almost all polymers tried a peroxy radical spectrum appeared in 5 minutes and its intensity approached a steady-state level after an hour or two. In many cases a broader spectral component also appeared, but more slowly.

Peroxy radical spectra

Peroxy radical spectra alone, with features corresponding to $g_{||} = 2.033$, $g_{\perp} = 2.004$, were given by polymers in the lower half of Table I. There were minor differences in spectral shape: for example, the peroxy radical derivative spectrum from poly(methyl methacrylate) had a

TABLE 1

Radical Concentrations, Spins/g, in Fluorine Treated Polymers

<u>Polymer</u>	<u>Broad</u>	
	<u>Component</u>	<u>RO₂</u>
Polyethylene, high pressure, powder	2.6×10^{18}	6×10^{17}
Polyethylene, linear, film	1.4×10^{18}	7×10^{17}
Polystyrene, fluff	2.9×10^{18}	3×10^{17}
Polyvinyl chloride, powder	1.4×10^{18}	N.D.
Polyvinylidene chloride copolymer, powder	1.3×10^{18}	N.D.
Polyhexafluoropropylene, fluff	8.9×10^{18}	N.D.
Polyoctafluoropentadiene, foam	5.6×10^{18}	low
Fluorinated graphite, CF, powder	1.1×10^{20}	absent
Polytetrafluoroethylene, film, 6 μm	0	N.D.
Polytrifluoroethylene, 26°C, powder	0	5.5×10^{16}
Polytrifluoroethylene, 56°C, fluff	0	3.2×10^{15}
Poly(vinylidene fluoride), film, 58 μm	0	8×10^{15}
Poly(vinylidene fluoride), film, 11 μm	0	5×10^{16}
Poly(vinyl fluoride), film, 0.1 mm	0	1.2×10^{16}
Hexafluoropropene-vinylidene fluoride copolymer, film	0	3.4×10^{15}
3,3-Trifluoropropene-tetrafluoroethylene copolymer, 64 mole % TFE, film	0	N.D.
Poly(methyl methacrylate), fluff	0	5.3×10^{17}
Cellulose, fiber	0	1.7×10^{16}

N.D. - Present but not determined

marked shallow minimum between the $g_{||}$ and the onset of the g_{\perp} region, while that from poly(vinyl fluoride) did not. Steady-state concentrations were in the range 3×10^{15} to 5×10^{17} spins per gram. In polytetrafluoroethylene the radical concentration soon began to fall and reached very low values in the course of several hours. The radicals observed in this spectrum were evidently due to the action of fluorine and oxygen on more reactive impurities which were gradually consumed. In polyhexafluoropropene also the initially intense peroxy radical part of the spectrum decreased drastically after two hours of fluorine treatment. Similar time-dependent behavior is reported for the chemiluminescence of PTFE samples under continued exposure to oxygen [14].

Comparison of two thicknesses of poly(vinylidene fluoride) film emphasized the shallow depth of the reaction zone. Pressed film of thickness 58 μm reached a concentration of 8×10^{15} spins per gram, while a thinner cast film, 11 μm , reached 5×10^{16} spins per gram; thus the number of spins was more nearly proportional to surface area than to volume, even in these relatively thin specimens. Concentrations of the peroxy radicals dropped to a small fraction of the steady maximum upon standing 15 hours at room temperature in nitrogen. They diminished to about the same extent in 15 min. at 40°C in nitrogen, in the few cases tried. In polytrifluoroethylene gradually heated to 50°C while continuing the flow of dilute fluorine, the concentration dropped and the spectrum also became narrower, as would be expected from motional narrowing [15]. This spectral narrowing is consistent with the observation of a mechanical loss tangent maximum at 45°C , 10Hz and its attribution to the glass transition of this polymer [16]. Other reports give the glass transition temperature at 32°C [17,18]. Admission of propylene at room temperature destroyed the peroxy radicals rapidly, with a half-life of about 15 min. at room temperature.

Crosslinking of hexafluoropropene-vinylidene fluoride copolymer and 3,3,3-trifluoropropene-tetrafluoroethylene copolymer in these experiments was shown by subsequent swelling and solubility tests, further detailed in Ref. 10 and 11. Cotton cellulose fibers, although expected to be highly reactive, had not yet lost all strength after 20 hours of exposure. In many of the polymers described above, an active role for hydrocarbon and fluorocarbon radicals is suggested by the observed instances of crosslinking in Refs. 10 and 11, but their presence is revealed only by their conversion to the peroxy radicals, which are apparently longer lived in all these experiments.

ESR spectra with a broad component:

Some polymers in Table 1 developed ESR spectra containing a broad component in addition to the peroxy radical part when treated with dilute fluorine. In addition a sample of fluorinated graphite, of approximate composition CF, exhibited a broad, intense ESR absorption in the absence of further fluorine treatments. In general, these spectra differed from polymer to polymer, although there was little or no spectral structure. Examples are shown in Fig. 1 and highest concentrations achieved are given in Table 1. The spectrum of fluorinated graphite, not shown, was broad,

covering about 150 mT overall, symmetrical, and not accompanied by an RO_2 spectrum. The spectrum of fluorinated polyhexafluoropropene was also broad, about 100 mT overall, but unsymmetrical and accompanied by an initially prominent RO_2 spectrum. The overall spectral widths of the fluorinated polyethylene and polystyrene in Fig. 1 are somewhat less than for cold irradiated polytetrafluoroethylene (about 40 mT), corresponding to $-CF_2\dot{C}FCF_2-$ and $-CF_2CF_2\cdot$ [19], and could be compatible with hyperfine interaction with one alpha and less than four beta fluorines, as suggested earlier [9].

The spectral widths for fluorinated poly(vinyl chloride), Fig. IE, and poly(vinylidene chloride), Fig. ID, are less than that for irradiated polytetrafluoroethylene but greater than values scaled from the irradiated unfluorinated polymers, which are 11.5 mT overall, 4.5 mT between derivative maxima for poly(vinyl chloride) [20] and 9.0 and 2.8 mT respectively for poly(vinylidene chloride) [21]. These data, taken alone, would be consistent with radical structures having chlorine atoms, and therefore fewer fluorine atoms, in alpha and beta positions. The spectrum of fluorinated polyoctafluoropentadiene, Figure IC, is strikingly like that reported for fluorine-treated polyhexafluorobutadiene [13]. This is perhaps reasonable as both initial polymers have internal double bonds, although the pentadiene polymer also has pendant vinyl groups [22]. Many of the polymers which had a broad spectral component acquired a substantial fluorine content (Table 2) or gained weight -- Poly(vinyl chloride), 28%; poly(vinylidene chloride), 27%; polyoctafluoropentadiene, 6% -- whereas the few hydro fluoro polymers examined did not gain weight appreciably [10,11].

TABLE 2
Elemental Analyses of Fluorine Treated Polymers

	Exposure, Hr.		%F	%C	%H
	25°C	60°C			
Polyethylene	8	0	23.7	39.4	5.8
Polyethylene	64	4	30.8	56.6	7.7
Polystyrene	6	0	14.2	77.9	6.2
Polystyrene	100	7	41.2	56.0	3.8
Polystyrene, heated to 130°C exposure	100	7	36.4	53.7	3.5

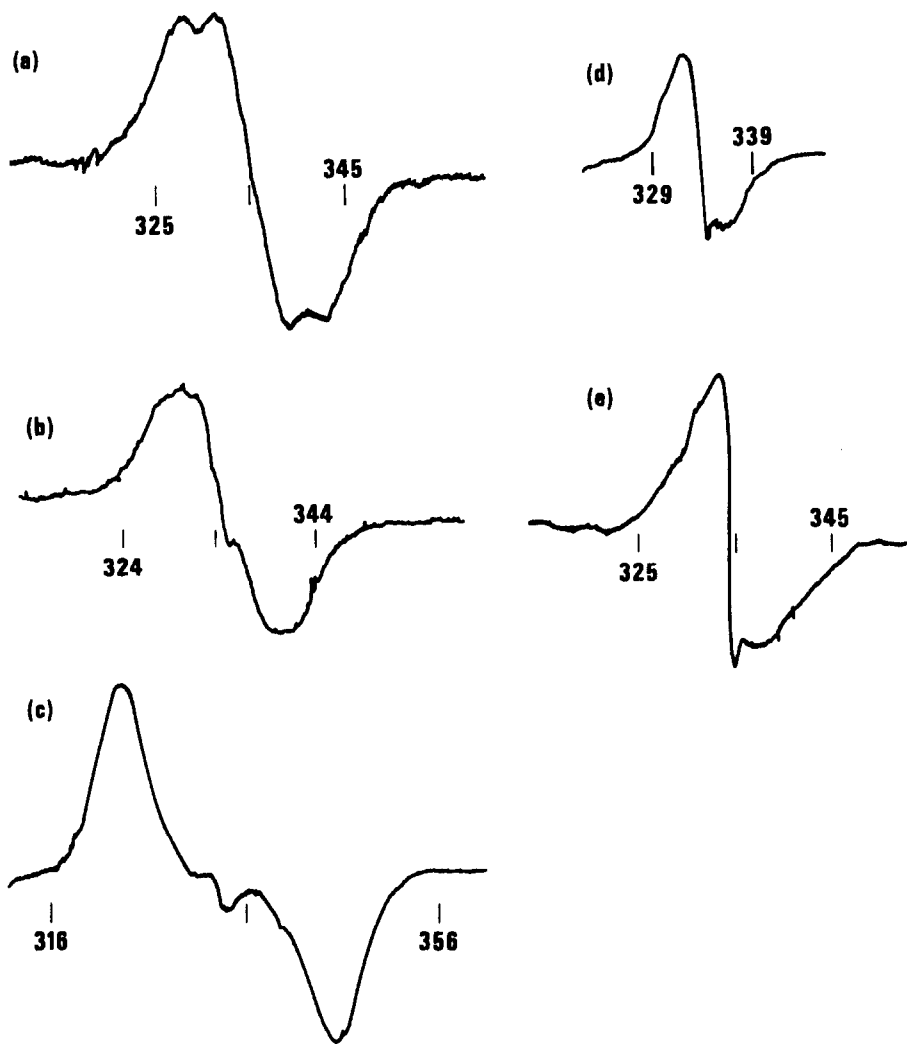


Figure I. ESR Spectra of Fluorine Treated Polymers Showing a Broad Spectral Component. A, polystyrene, after 60°C heating in vacuo, at 9403 MHz; B, linear polyethylene, after 60°C heating in vacuo, at 9393 MHz; C, polyperfluoropentadiene, 9374 MHz; D, vinylidene chloride copolymer, fluorinated at 56°C , spectrum at 56°C , 9390 MHz; E, poly(vinyl chloride), fluorinated at 56°C , spectrum at 37°C , 9401 MHz. Numbers on lines, nominal magnetic field in millitesla.

The broad spectral component did not disappear under conditions usual for radical destruction. Injection of oxygen, although it increased the formation of peroxy radicals while fluorine was flowing, did not convert the performed broad spectral component into a peroxy radical spectrum; and injection of propylene, which rapidly destroyed the peroxy radical spectrum, had no effect on the broad component. The broad spectral component did not decrease over several days at room temperature, even when exposed to oxygen, but disappeared slowly upon heating in nitrogen, about half the intensity being lost in several hours at 100°C for polystyrene and at 80°C for linear polyethylene. The kinetics of disappearance were complicated. A small residue remained at temperatures up to 130°C for polyethylene, and attempts to fit first order, second order and $\sqrt{\text{time}}$ diffusion kinetics at any temperature were unsuccessful.

A search for transition metals which may be responsible for the broad component of the spectrum was made by neutron activation analysis, with results summarized in Table 3. In the case of poly(vinyl chloride) copper is indicated, in sufficient amounts to account for the full ESR spectral intensity. The finding of copper is rendered less certain by the possible interference of sodium. Another possible objection to the attribution to copper is that the reported ESR spectrum of anhydrous CuF_2 [23], although fairly symmetrical is broader (40 mT between points of half maximum absorption) than that observed in the polystyrene and polyethylene specimens, while the acid fluoride $\text{CuF}_2 \cdot 5\text{HF} \cdot 5\text{H}_2\text{O}$ has a highly asymmetrical spectrum [24]. The neutron activation detection limit for iron is relatively high, but again not sufficient to account for the full ESR spectral intensities in Table 1. The ESR spectrum of hydrated FeF_3 [25] is perhaps narrow enough to be compatible with those displayed in Figures 1A and 1B, but spectra of anhydrous fluorides of iron are not known. Anhydrous NiF_2 can be excluded as its large zero field splitting would make it undetectable at 9000 MHz [26,27]. Despite the insufficient evidence, it seems likely on balance, especially because of the kinetics of disappearance, that the broad spectral component is due to unknown transition metal compounds and is not related to the mechanism of fluorination. As exceptions, the polyoctafluoropentadiene may well contain radicals formed by addition to the double bond, and the CF fluorinated graphite has an ESR spectrum resembling that of some carbon black samples. Possibly in the latter instance, despite the dazzling white appearance of the product, isolated regions of extensively conjugated radical structure could exist in the interior of particles.

TABLE 3

Transition Metals and Spins Per Gram in Fluorine Treated Polymers

Polymer	Mn, μg/g	Cu, μg/g	Cu Equivalent Spins/g	ESR Broad Component Spins/g
Polystyrene	0.3	22	2.2×10^{17}	2.9×10^{18}
Polyethylene, linear	0.28	6.6	6×10^{16}	1.4×10^{18}
Poly(vinyl chloride)	0.11	205	2×10^{18}	1.4×10^{18}
Poly(vinyl chloride) before fluorination	0.3	5.5	5×10^{16}	0
Poly(vinylidene chloride)	0.34	11.5	1.1×10^{17}	1.3×10^{18}

Based on neutron activation analyses. All samples were negative for Cr, Co, Fe and Ni at detection levels of 1, 0.1, 20 and 20 μg/g respectively

CONCLUSIONS

It has been shown that ESR spectra characteristic of peroxy radicals appeared rapidly in all hydrogen-containing polymers examined when treated with dilute fluorine. The origin of these radicals is obviously the reaction of hydrocarbon and fluorocarbon radicals, at undetectably low steady-state concentrations, with oxygen which is always present as an impurity in commercial fluorine. These precursor radicals are the intermediates for the fluorine substitution, crosslinking, and chain scission variously observed. The precursor radicals must occur at relatively low concentrations and have short lifetimes in the steady-state of reaction, as more peroxy radicals are not produced by flushing out fluorine and subsequently admitting oxygen. The broad spectral component observed in some polymers exposed to fluorine does not react with ordinary radical scavengers such as propylene and oxygen, and is probably not due to a fluorocarbon radical but to unknown transition metal fluorides. Likely exceptions are the broad spectrum of fluorinated graphite, which may come from highly conjugated radicals like those in carbon black, and the spectrum of fluorinated polyoctafluoropentadiene, which closely resembles that in fluorinated polyhexafluorobutadiene, and may plausibly be formed by addition of a fluorine atom

to an internal or vinylic double bond. In poly(vinylidene fluoride) films of thickness 11 and 58 μm the radical contents were nearly proportional to surface rather than volume, in agreement with earlier reports [6] of a shallow depth of penetration.

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