

4 (sealed ampule at 250 °C). The alternative mode of cleavage of the cyclobutane is followed, however, and the only volatile products are the diene **18**⁸ and α -campholenic aldehyde (**19**).¹⁷

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Simultaneous Fluorination and Functionalization of Hydrocarbon Polymers

Sir:

A thermally and chemically resistant fluorocarbon polymer which supports isolated reactive functional moieties would find much utility as a catalyst support, as a template for biochemical or other synthetic applications, and as membranes and separators for chloro alkali cells and batteries. We report some results in which existing hydrocarbon polymers are simultaneously fluorinated and functionalized using various mixtures of fluorine and oxygen to produce a polytetrafluoroethylene-like backbone with varying degrees of functionalization, 5-60% acid fluoride to monomer groups.

There has for several years in our laboratory been an interest in the reactions of mixtures of oxygen and fluorine. Previously, we have used such mixtures as reagents to oxidize inorganic polymers such as boron nitride.¹ Earlier work by Miller and Dittman showed that mixtures of fluorine and oxygen could, for example, convert tetrachloroethylene to 1,1-dichloro-1-fluoroacetyl chloride.² Miller described the process as a "fluorine sensitized oxidation" process. Because our process differs in that it converts hydrocarbon polymers to functional fluorocarbon polymers we have for brevity called the process "oxy-fluorination".³ The process of oxy-fluorination was discovered independently by Manley.⁴ This process is not limited to polymers, but has been used successfully to oxy-fluorinate neopentane and 1,4-dioxane⁵ and to convert *n*-alkanes to perfluoro acids and diacids.⁶

The results of the oxy-fluorination of polyethylene (low density) and polypropylene under varying conditions are pre-

Table II. Run 5 (Table I)^a

polyethylene wt, g	He, cm ³ /m	F ₂ , cm ³ /m	O ₂ , cm ³ /m	Time, days
2.28	40	2.0	0.1	1
	40	4.0	0.2	1
	40	5.0	0.25	1
	20	1.0	0	5
	5	1.0	0	1
	0	1.0	0	4

^a Yield 6.93 g, ν_{CO} 1882 cm⁻¹, CFO content 0.53×10^{-3} mol/g.

The relationship between oxygen introduced and the COF content (polypropylene)

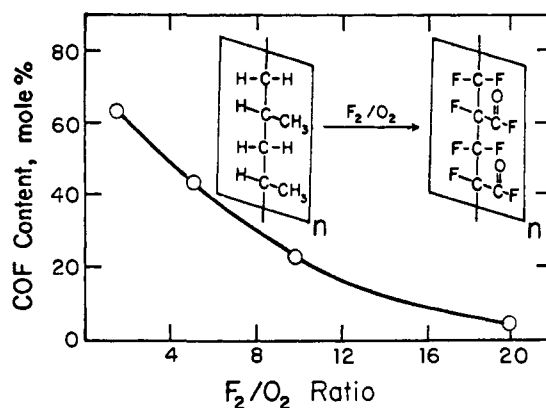


Figure 1.

sented in Table I. A typical run (5) is shown in Table II: Initial low concentrations of F₂/O₂ in helium are gradually increased to maximum concentration at zero helium flow. Finally, pure fluorine was admitted to remove residual C-H bonds. Overall pressures and temperatures were ambient room values and no attempt was made to decrease or optimize reaction time. All polymers were studied initially in the form of finely divided (>120 mesh) powder form. In subsequent work 5-mil films were used with very little change in the degrees of functionalization. The density of the low density polyethylene starting material, prepared by the method of Hale,⁷ was 0.91.

It can be seen from the F₂:O₂ ratios and the COF content (Figure 1) that the degree of functionalization is directly related to the F₂:O₂ ratio. After the reaction, the acid fluoride groups have strong carbonyl infrared stretches at ~ 1880 cm⁻¹ and, after hydrolysis, an acid carbonyl is a prominent infrared feature. The acid fluoride groups were assayed by careful titration with HCl after the sample had been hydrolyzed, vac-

Table I

Run	Wt, g	F ₂ :O ₂ , cm ³ /m	Time, days	COF, mol/g	ν_{CO} , cm ⁻¹	Anal., %		Mp, °C
						C	F	
Polyethylene								
1	0.52	1.0:1.0	5	4.9×10^{-3}	1850			>360
2	10.36	1.0:0.5	17	3.16×10^{-3}	1880	26.83	66.78	>360
3	10.84	2.0:0.4	25	1.8×10^{-3}	1880	25.62	68.29	>360
4	1.53	2.0:0.2	9	0.78×10^{-3}	1880			>360
5	2.28	2.0:0.1	13	0.53×10^{-3}	1882			>360
Polypropylene								
6	1.0	2.0:1.0	9	4.66×10^{-3}	1860			110 ^a 95 ^a
7	5.3	2.0:0.4	35	3.14×10^{-3}	1875	25.79	69.23	307 ^a 20 ^a
8	4.0	2.0:0.2	22	1.53×10^{-3}	1880	26.83	68.25	307 ^a 305 ^a
9	0.6	2.0:0.1	17	0.44×10^{-3}	1875			340 ^a

^a Decomposes.

Table III. Reaction of the Functionalized Polymers^a with Alcohols and Aniline

	Reactant			
	MeOH	EtOH	<i>n</i> -BuOH	Aniline
Polymer 1				
Yield, %	57.1	44.1	56.0	57.7
IR (C=O), cm ⁻¹	1775	1775	1770	1770
Mp, °C	320 (dec)	317 (dec)	330 (dec)	310 (dec)
Polymer 2				
Yield, %	82.3	76.3	82.2	89.2
IR (C=O), cm ⁻¹	1775	1775	1775	1775
Mp, °C	310 (dec)	305 (dec)	354 (dec)	<i>b</i>
Polymer 3				
Yield, %	54.9	50.5	68.0	63.3
IR (C=O), cm ⁻¹	1775	1773		1695
Mp, °C	320 (dec)	<i>b</i>	<i>c</i>	210 (dec)
Polymer 4				
Yield, %	81.8	73.2	76.0	73.0
IR (C=O), cm ⁻¹	1780	1775		1700
Mp, °C	<i>b</i>	<i>b</i>	<i>c</i>	<i>b</i>
Polymer 5				
Yield, %	96.5	96.7	96.6	98.1
IR (C=O), cm ⁻¹	1780	1780	1780	1710
Mp, °C	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>

^a Polymer 1, oxyfluorinated polypropylene (F₂:O₂, 5:1); polymer 2, oxyfluorinated polypropylene, (F₂:O₂, 10:1); polymer 3, oxyfluorinated polypropylene (F₂:O₂, 2:1); polymer 4, oxyfluorinated polypropylene (F₂:O₂, 5:1); polymer 5, oxyfluorinated polypropylene (F₂:O₂, 20:1).

^b Did not melt below 360 °C. ^c Tacky material.

uum dried, and neutralized with a measured amount of NaOH. All of the polyethylene-derived polymers were completely fluorinated and showed good thermal stability as evidenced by IR, elemental analyses, and DSC-TGA data.

The polypropylene-derived polymers showed lower melting points and the more highly functionalized polymers reduced thermal stability. The significantly lower stability of the polymer produced in run 6 is probably attributable to the presence of residual carbon-hydrogen bonds which are seen as a weak band at 3000 cm⁻¹ in the infrared. This product decomposed at 110 °C with evolution of gas. The remaining polymers appear to be completely fluorinated as determined by IR and elemental analysis.

The oxy-fluorinated polymers would be expected to react with a variety of organic, inorganic, and organometallic compounds. Derivatives of each functionalized material have been prepared with CH₃OH, C₂H₅OH, *n*-BuOH, and aniline. The efficiency of the derivatization process ranged from 44 to 98%, as can be seen in Table III. The substituted polymers were characterized by infrared spectra, melting points, and elemental analyses.

The functional polymers prepared by the oxy-fluorination process are promising for use as templates, catalyst supports, or ion-exchange resins. The most highly functionalized polymers were very hygroscopic and in aqueous solution had about the same refractive index as water. Because a small amount of fragmentation has occurred in the original polymer as well as some degree of cross-linking, a wider range of molecular weights would be expected following oxy-fluorination. Narrowing the molecular weight distribution would require solvent extraction or other refinement techniques. It is worthwhile to note that oxy-fluorination of linear polyethylene fails to produce significant functionalization. This implies that acid fluoride groups are produced primarily by oxidation of pendant methyl or other alkyl groups in low density polyethylene or in polypropylene rather than from cleavage of carbon-carbon bonds. Up to 60% of the pendant methyl groups in polypropylene are converted to acid fluoride sites. Although the degree of functionalization is about the same in the low density polyethylene, the percentage of available pendant alkyl groups

converted to acid fluorides is higher. It is probable that the amorphous nature of low density polyethylene permits a higher fluorine and oxygen diffusion rate than the more crystalline polypropylene. Steric factors may also favor more complete functionalization of polyethylene.

The fact that functionalization of polymers and small molecules is observed to occur predominately on terminal (methyl) carbon atoms does not imply that the oxy-fluorination reaction is truly selective. Although the reaction mechanism has not been studied in detail, it is undoubtedly a free-radical process. Molecular oxygen reacts spontaneously with the fluorocarbon-hydrocarbon radicals generated by fluorine during the fluorination process. Acid fluorides are retained on terminal carbon atoms because they are stable in 1 atm of elemental fluorine. Hypofluorites, which may be short-lived intermediates of oxygen reactions with methylene radical sites along the carbon chain, are not observed in the functionalized polymers. It is probable that, if they are intermediates, they are cleaved and removed by the excess elemental fluorine.

The preparation of similar types of polymers with a more regular degree of functionalization has been achieved by direct fluorination of functional polymers which were prepared by copolymerization of other monomers. For example, the copolymer of acrylic acid/vinyl chloride (8.1 mol % acrylic acid) was fluorinated producing a completely halogenated polymer, COF content 4.0×10^{-4} mol/g, ν_{CO} 1873 cm⁻¹. Found: C, 22.36; F, 58.94. The fluorinated polymer, unlike the unfluorinated polymer, showed good thermal properties and improved resistance to hot alkali. It is presumed to have a backbone structure intermediate between polytetrafluoroethylene and polychlorotrifluoroethylene. In this case some fragmentation occurs but cross-linking is not so great a problem with the low ambient oxygen levels present in commercial fluorine (1% maximum).

In this communication two methods for producing functional polymers with fluorocarbon backbones are presented. The high reactivity of the functional groups coupled with the chemical and thermal resistance of the polymer backbones makes these substances ideal for uses requiring isolated sites of high reactivity distributed over a chemically inert backbone. We have

prepared, using this technique, a number of different functionalized fluorocarbon polymers with varying physical, thermal, and chemical properties which should compliment or compete in applications established for the sulfonic acid functionalized fluorocarbon polymer "Nafion" which has been previously reported.⁸

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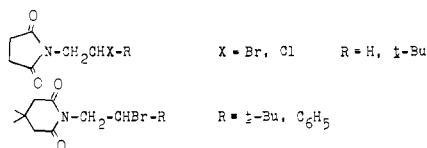
Addition Reactions of Imidyl Radicals with Olefins and Arenes

Sir:

Hydrogen abstracting reactions of succinimidyl radical have been described.^{1,2} We report here the facile radical-chain additions of NBS to both alkenes and arenes, and also selectivities different from those known from carbon radical chemistry.

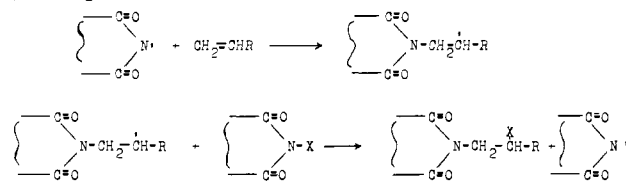
The addition reactions are carried out using a 3:1 mol ratio of olefin/*N*-haloimide in methylene chloride, chloroform, or carbon tetrachloride as solvents. These reactions may be photoinitiated through Pyrex using a medium-pressure mercury arc lamp as a light source, or thermally initiated with benzoyl peroxide at reflux temperatures; both methods are effective, yields being 40–80%. In the absence of initiation no reaction occurs.³

The products (shown below) of alkene-haloimidyl radical-chain reactions have been isolated as pure solids, and structures proven with ¹H NMR spectroscopy. Chromatography over alumina was employed in the purifications, attended by hydrolysis to the corresponding alcohol in the case of the styrene adduct only.

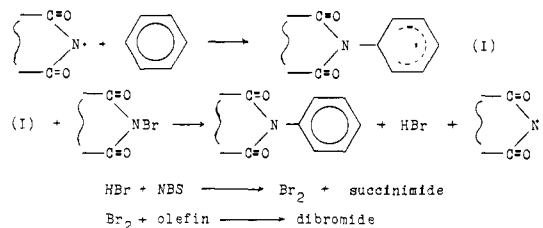


The failure of dark reactions and the absence of rearrangement products in the reactions of *tert*-butylethylene rule

Scheme I



Scheme II



out an ionic reaction mechanism. The presence of the imidyl moiety on the terminal atom of *tert*-butylethylene and styrene adducts make clear the chain sequence shown in Scheme I.

In methylene chloride solvent olefins with allylic hydrogens react similarly, the additions and the allylic substitutions being closely competitive processes. For example cyclohexene and *N*-chlorosuccinimide react to give ~50% adduct and ~50% substitution products 3- and 4-chlorocyclohexene.

The same reaction conditions as above are effective for substitution in arene systems;⁴ for example, reactions carried out with benzene and *tert*-butylethylene in 6:1 ratio results in 1:1:1 mol ratio *N*-phenylated imide, imide, and dibromo adduct of *tert*-butylethylene (Scheme II); in these circumstances there is no loss of NBS to ring-opening product β -bromopropionyl isocyanate. Also, small amounts (~10%) of the *tert*-butylethylene-NBS adduct are obtained. The yield of *N*-phenylsuccinimide is 45% based on NBS consumed; the theoretical yield is 50%.

Employing the same reactant ratios, similar results are obtained with substituted aromatics, for example, *tert*-butylbenzene, chlorobenzene (45% *o*-, 28% *m*-, 28% *p*- with *N*-bromo-3,3-dimethylglutarimide (NBDMG)), *p*-dichlorobenzene, and naphthalene (66% α -, 33% β - with NBS). With anthracene ring-brominated products occur along with imidation products. Aromatic substrates possessing benzylic hydrogens, such as toluene and *p*-xylene, yield substantial amounts of benzylic bromide product. For example, toluene and NBDMG at 65 °C yield a product mixture consisting of 65% benzyl bromide and 35% imidation product (48% *o*-, 31% *m*-, and 21% *p*-). In these cases, however, use of lower reaction temperatures (0 °C or lower) shifts the product composition in favor of ring imidation. The reaction of toluene with NBDMG at -20 °C gave a mixture, of which more than 80% was imidation product.

In accord with considerations discussed elsewhere,⁵ the chemistry described here is attributed to excited-state imidyl radicals, S_2 , which have been identified with the σ_O or σ_N states.⁶ The intermediacy of a σ_N imidyl radical seems most likely in view of the addition product structures, with the nitrogen atom of the imidyl moiety bonded to one of the carbons of the olefin or arene.

The relative reactivities of these S_2 species has been probed with two types of competition systems, C-H abstraction vs. alkene addition and alkene addition vs. arene addition.

In the competition between neopentane and addition to *tert*-butylethylene (TBE), with succinimidyl radical, ($k_{(\text{CH}_3)_4\text{C}}/k_{\text{TBE}}$) = 0.15, or 0.04 when calculated on a per methyl group basis. The value of Cl \cdot choosing between abstraction at the methyl position of 1-butene and addition to the double bond, ($k_{\text{abstr}}/k_{\text{addn}}$) = 0.053.⁷ The concordance of