

# The Direct Fluorination of a Porous Functionalized Polymer

JOHN D. HEWES\*, SEAN CURRAN, and EDGAR A. LEONE

AlliedSignal Inc., Research and Technology, P.O. Box 1021, Morristown, New Jersey 07962-1021

## SYNOPSIS

Macroporous sulfonated polystyrene ion exchange resin was reacted with elemental fluorine in a liquid-phase suspension reactor at low temperature. This method gave retention of the bulk structure of the resin bead and resulted in a space-selective distribution of fluorine across the resin bead cross-section, as determined using  $^{19}\text{F}$  secondary ion mass spectroscopy (LMI-SIMS). The polymer modification was additionally characterized using x-ray photoelectron spectroscopy, photoacoustic IR spectrophotometry,  $^{19}\text{F}$ , and  $^{13}\text{C}$  MAS NMR spectrometry, and mercury porosimetry. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Polymer surface modification by direct fluorination is gaining popularity.<sup>1</sup> Although the high reactivity and poor chemical selectivity of elemental fluorine has restricted work on the direct fluorination of functionalized polymers,<sup>2</sup> the fluorination of organic polymer-supported sulfonic acids, i.e., ion exchange resins, was previously attempted with some success.<sup>3</sup>

Electronic effects induced by fluorine atoms on the carbon backbone of monomeric organic acids are known for the increase in Brønsted acidity over the nonfluorine-containing hydrocarbon analogs. Our attempt to fluorinate polymer-supported acids stems from an interest in increasing the acid strength of polymer-supported organic acids<sup>4</sup> by directly incorporating fluorine atoms into hydrocarbons such as sulfonated polystyrene ion exchange resins. Inexpensive, porous analogs to polymeric perfluorocarbon sulfonic acids, such as DuPont Nafion<sup>TM</sup>,<sup>5</sup> could be produced using such a process.

Historically, gas-phase direct fluorination techniques are based on the "LaMar" reactor,<sup>6</sup> wherein dilute fluorine gas is applied to a sample that is loaded inside a tube reactor. This report discusses improved fluorination techniques, applied to the treatment of various polymer substrates, that were developed from research on polymer surface modification. Reported herein are the chemical and

physical characterizations of ion exchange resins that have been fluorinated with physical and chemical selectivity. The observed enhancement of the acid strength and the catalytic selectivity of the polymer-supported acids shall be reported elsewhere.

## EXPERIMENTAL

### Materials and Methods

Macroreticular ion exchange resin M-32 (Dow Chemical Company) was washed and converted to the sodium form using, sequentially, copious amounts of deionized water, 1 M NaOH, 1 M HCl, 1 M NaOH, deionized water, methyl alcohol, and dichloromethane at room temperature. Resins were dried<sup>1b,7</sup> to a moisture content of 0.1 wt-%, as verified by Karl-Fisher titration, under a flow of purified nitrogen prior to vacuum drying at 90°C/10<sup>-3</sup> Torr, and were stored under nitrogen in Schlenk tubes or in sealed glass ampules. Fluorine gas (Air Products and Chemicals, 98%) was purified using a sodium fluoride trap (Matheson) and controlled using Hastings Model CST-M mass flow controllers. Waste fluorine was scrubbed using granular aluminum oxide (Alcoa Chemicals Co.) traps. *Fluorine gas is a highly reactive and toxic gas that should be used only by trained personnel knowledgeable in its safe use and in possession of proper equipment and safety procedures.* Nitrogen was obtained as boil-off and passed through a molecular sieve trap prior to use. Trichloro-fluoromethane (AlliedSignal Genetron-11)

was dried over magnesium chloride and vacuum transferred prior to use.

For the liquid phase fluorination reactions, a glass-jacketed FEP tube 3.75 cm  $\times$  1.25 m, equipped at the bottom with a 20  $\mu$  Monel sparger and at the top with a gas outlet port, was charged with 500 mL trichlorofluoromethane and 80 g sodium-form resin under a flow of nitrogen. The reaction tube was cooled to  $-45 \pm 3^\circ\text{C}$  using an external thermostated methanol bath. The 100 standard cubic centimeters per minute (sccm) flow of 2% v/v fluorine/nitrogen mixture was introduced into the suspension following a 30-min nitrogen purge. After 5 days, the suspension was purged with nitrogen for 30 min, warmed to ambient temperature, and the resin beads were drained from the bottom of the reactor. To prevent fracture of the anhydrous resin beads upon hydration, the resin was gradually moistened with water using a water vapor humidifying chamber after the residual  $\text{CCl}_3\text{F}$  had been removed under a flow of nitrogen. When thoroughly water wet, the resin was placed into a glass column and washed sequentially with deionized water, 1 M NaOH, 1 M HCl and copious amounts of deionized water before drying to 0.1 wt-% water at  $90^\circ\text{C}/10^{-3}$  Torr. Elemental analysis:<sup>8</sup> 47.48% C, 3.87% H, 12.72% S, 14.10% F vs. unfluorinated control: 51.40% C, 5.20% H, 14.49% S.

Gas-phase ("LaMar") fluorination experiments were conducted for comparison. The reaction chamber consisted of a 4"  $\times$  11"  $\times$  14" welded Monel box with a Viton-sealed lid. The resin beads were distributed uniformly as a monolayer onto a horizontal stainless steel tray that was subsequently inserted into the box. The reaction chamber was chilled to ca.  $-60^\circ\text{C}$  using external dry ice. After being purged with 200 sccm nitrogen for 24 h, a 100 sccm flow of 2% v/v fluorine/nitrogen mixture was introduced for 48 h, and then the chamber was flushed with nitrogen while warming to room temperature. The substrate was removed and water-wetted as described above. Elemental analysis:<sup>8</sup> 48.91% C, 4.14% H, 12.95% S, 10.37% F.

### Characterization

X-ray Photoelectron Spectroscopy (XPS) was performed on a VG ESCALAB Mark II surface analysis system. An Al  $K\alpha$  x-ray source (1486.6 eV) was used along with a triple channeltron electron detector system. The XPS data were corrected for escape depth and photoionization cross-section. The  $^{19}\text{F}$  liquid metal interface-secondary ion mass spectrometry (LMI-SIMS) was performed on the same

instrument using a Ga liquid metal ion source at an accelerating voltage of 10 KeV. The resin beads were manually cut in half and mounted onto a sample stub using double-sided adhesive tape. Charge neutralization was used with a low energy electron flood gun to obtain steady secondary ion emission.

Mercury porosimetry was performed on a Micromeritics Autopore Model 9210 using procedures recommended by the manufacturer.

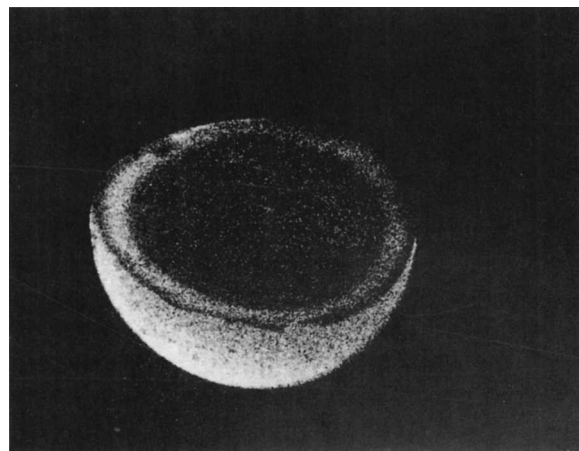
Elemental analyses were performed by Quantitative Technologies, Bound Brook, NJ. Oxygen content was measured indirectly.

$^{13}\text{C}$  and  $^{19}\text{F}$  Magic Angle Spinning (MAS) NMR experiments were acquired using a Chemagnetics CMX-300 operating at 75 MHz for the  $^{13}\text{C}$  nucleus. Samples were chilled with liquid nitrogen and ground for pellet preparation.  $^{13}\text{C}$  NMR spectra were acquired via cross-polarization with 5  $\mu\text{s}$   $90^\circ$   $^1\text{H}$  pulses, using either 2- or 5 ms contact times (to emphasize protonated or nonprotonated carbons, respectively) and 2 s cycle times. Selective spectra of "nonprotonated carbons" were acquired via dipolar dephasing (DD).

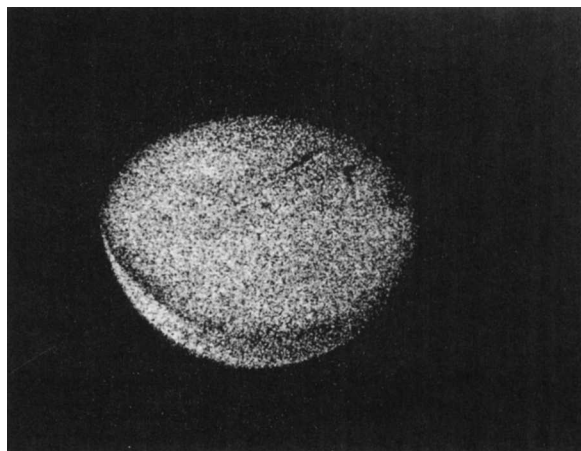
The single beam photoacoustic IR spectra of the resin samples were measured on a Matteson Cygnus 100 FT-IR spectrometer at  $4\text{ cm}^{-1}$  resolution using a MTEC 200 photoacoustic detector and were ratioed to a carbon black reference.

## RESULTS AND DISCUSSION

The spacial distribution of fluorine in the resin bead was observed using  $^{19}\text{F}$  LMI-SIMS on substrate



**Figure 1**  $^{19}\text{F}$  LMI-SIMS cross-sectional profile of fluorine distribution from a resin bead treated in the liquid-phase suspension reactor.



**Figure 2**  $^{19}\text{F}$  LIM-SIMS cross-sectional profile of fluorine distribution from a resin bead treated the "LaMar" type gas-phase reactor.

fluorinated in both the liquid-phase and gas-phase reactors. The liquid-phase suspension reaction gives a selective profile of fluorine across the resin bead cross-section (Fig. 1) to yield an orange-peel effect of fluorinated polymer.

This phenomenon contrasts sharply with the results of the gas-phase reaction, which is characterized by a uniform distribution of fluorine atoms across the entire resin bead cross-section (Fig. 2), and, presumably, throughout the volume of the bead.

The elemental composition of the resin beads fluorinated in the liquid-phase reactor were determined using x-ray photoelectron spectroscopy (Table I), and agrees with earlier findings.<sup>1c</sup> The surface of the resin bead from the liquid-phase reactor shows the addition of 47.4 at-% fluorine atoms to the polymer chain and represents a distribution of approximately one fluorine atom per carbon atom. The outer bead surface of the liquid phase reaction is slightly more fluorinated than that found from the gas phase reaction. The loss of sulfur, presumably through formation of volatile  $\text{SF}_6$ , is noted by the decrease from the observed S/C ratios in the untreated vs. fluorinated resin; a ratio of 0.037 in the liquid-phase

reactor and 0.073 in the gas-phase fluorinated resin indicates greater loss of sulfur in the liquid-phase reaction. The overall loss of oxygen atoms is indicated by a decrease in O/C ratio in the fluorinated samples. The decrease in oxygen can be accounted for in the loss of sulfonic acid groups; however, the ratio is complicated by the fact that the fluorinations and subsequent workup were not conducted in thoroughly deoxygenated solvents. The presence of oxygen during the fluorination of hydrocarbons has been noted<sup>1b</sup> to lead to the formation of oxygenates and in reduced free radical-generated crosslinking.

Changes in pore size and distribution were determined by mercury porosimetry. The pore volume increases from  $0.325 \text{ cm}^3/\text{g}$  in the control to  $0.361 \text{ cm}^3/\text{g}$  in the liquid-phase reaction and  $0.372 \text{ cm}^3/\text{g}$  in the gas-phase reaction, as shown in Table II.

The pore area increases slightly upon fluorination, as well. The depletion of crosslinking upon fluorination results in a loss of mechanical strength that parallels the increased pore size: the gas-phase reaction results in resin beads that can be manually crumbled. A decrease in bulk density and skeletal density may be attributed to loss of the sulfonic acid groups, despite the increases expected for fluorine atom incorporation.

The  $^{19}\text{F}$  MAS NMR spectra were characterized by very weak, broad C-F peaks at low field. Typically, a C-F resonance in the  $^{13}\text{C}$  MAS NMR experiment would appear in the 70–100 ppm range and a  $\text{CF}_2$  resonance would appear in the 115–130 ppm range. The new nonprotonated carbon atoms at 148 ppm observed in the spectra of the liquid-phase fluorinated resin beads can be attributed to the fluorinated aromatic ring carbons. Based on previous experience with other fluoro-polymers, this peak would be quite broad, as observed, and would likely also be observable in a dipolar dephasing (DD) experiment. The observed downfield shift is consistent with ring fluorination but inconsistent with backbone fluorination. In fact, if the backbone itself had been fluorinated, we would expect new aliphatic peaks downfield from the styrene/divinyl-benzene backbone resonances, which were not seen.

**Table I** Elemental Composition of Fluorinated and Unfluorinated Resin Bead Surfaces by X-Ray Photoelectron Spectroscopy (Atom-%)

Sample	C	O	S	F	O/S	O/C	F/C	S/C
Unfluorinated	67.0	24.4	8.6	—	2.83	0.365	—	0.129
Gas phase fluorinated	45.9	12.5	3.3	38.3	3.75	0.272	0.83	0.073
Liquid phase fluorinated	42.6	8.4	1.6	47.4	5.31	0.196	1.11	0.037

**Table II Results of Mercury Porosimetry on Fluorinated and Unfluorinated Resin Beads**

Sample	Pore Volume (dL/cm <sup>3</sup> )	Pore Area (m <sup>2</sup> /g)	Average Pore Diameter (μm)	Bulk Density (g/cm <sup>3</sup> )	Skeletal Density (g/cm <sup>3</sup> )
Untreated	0.325	48	0.027	1.08	1.67
Liquid phase	0.361	58	0.025	1.02	1.54
Gas phase	0.372	58	0.026	0.99	1.56

The photoacoustic infra red spectra, obtained by subtraction of the spectra of untreated from treated resin beads, showed new resonances at 2920 (w) ( $\nu_{C-H}$ ), 2360 (w, doub), 1730 (m, br), 1470 (w), 1420 (w), 1400 (w, br) ( $\nu_{C=C}$ ), 1340 (sh,w), 1180 (st, br) ( $\nu_{C-F}$ ), 900 (w), 820 (w). The coincidental overlap of the sulfonic acid groups and the C—F bands at 1350–1000 cm<sup>-1</sup> precluded easy determination of acid strength by observation of  $\Delta\nu_{SO_3}$ .<sup>9</sup>

## CONCLUSION

Liquid-phase methods lead to a more selective distribution of fluorine on the resin matrix and reduces the significant loss of mechanical strength encountered by previous studies<sup>3d-e</sup> utilizing LaMar gas-phase techniques or modifications thereof. Our results show that the liquid-phase technique results in the fluorination of only the outer layer of the resin bead (an "orange peel" effect). The limited solubility of fluorine in chlorofluorocarbon solvents<sup>10,11</sup> apparently controls this spacial selectivity: when the individual resin beads are saturated with solvent, ready diffusion of fluorine gas into the interior is inhibited. The subambient temperatures and the low surface tension and high thermal conductivity of the liquid enhance the selectivity by removing the heat of reaction with the fluorine. In effect, the reaction is at the gas–solid interface; however, it is strongly mediated by the liquid phase present. The use of diluents having high thermal conductivity for vapor-phase direct fluorination was recently suggested elsewhere.<sup>11</sup> In contrast, the gas-phase, or LaMar, reaction of fluorine with polymers has limited site selectivity that can be determined only by the (rapid) diffusion of the gases through the pores to the interstitial areas of the beads. An attempt to reproduce a published,<sup>3e</sup> intermediate, approach using very high gas flow rates within a suspension reactor, however, gave results consistent with the gas-phase and not the liquid-phase technique.

Finally, the MAS NMR data indicate that the initial fluorination product is a fluorinated aromatic ring, not the backbone as suggested elsewhere.<sup>3d</sup> The exact position of the fluorine atom incorporation in polymers has not been discussed in the literature, although substitution patterns for monomeric species have been discussed.<sup>13</sup>

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