

Synthesis and Evaluation of Hexafluorodimethylcarbinol Functionalized Polymers as Microsensor Coatings

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SYNOPSIS

Polystyrenes, polyacrylates, and poly(3,4-isoprenes) incorporating the hexafluorodimethylcarbinol functionality have been synthesized, characterized, and tested as microsensor coatings on a surface acoustic wave (SAW) device for dimethyl methylphosphonate (DMMP) vapor absorption sensitivity. The syntheses involved monomer functionalization and polymerization or hexafluoroacetone reaction with preformed polymer. All fluoroalcohol functionalized polymer coatings displayed sub parts per million level sensitivity with the slope of the absorption isotherm steepest at low DMMP concentrations. The order of sensitivity for the isomeric polystyrene fluoroalcohols (*meta* > *para* ≫ *ortho*) paralleled that of the relative free hydroxyl to hydrogen-bonded hydroxyl content. Strong hydrogen bonding between the fluoroalcohol polymers and DMMP vapor was observed by IR spectroscopy. Acylation of the fluoroalcohol group markedly reduced the DMMP sensitivity.

INTRODUCTION

If a polymeric coating can be identified with a highly sensitive, selective, and reversible absorption for a particular vapor, it will readily find application as a key component of a chemical microsensor. In designing coatings for this application, one strategy is to incorporate a structural feature into the coating that will promote a molecular interaction directed at a particular vapor. Such interactions have included hydrogen bonding,^{1,2} transition-metal complexation,^{3,4} guest-host interactions,⁵ Diels-Alder adduct formation,⁶ and combined solubility-related interactions.⁷ Reviews have periodically appeared describing and cataloging a variety of electronic substrates and vapor-coating combinations.⁸ However, very little has been reported involving sensor response to systematic variations in the coating structure.

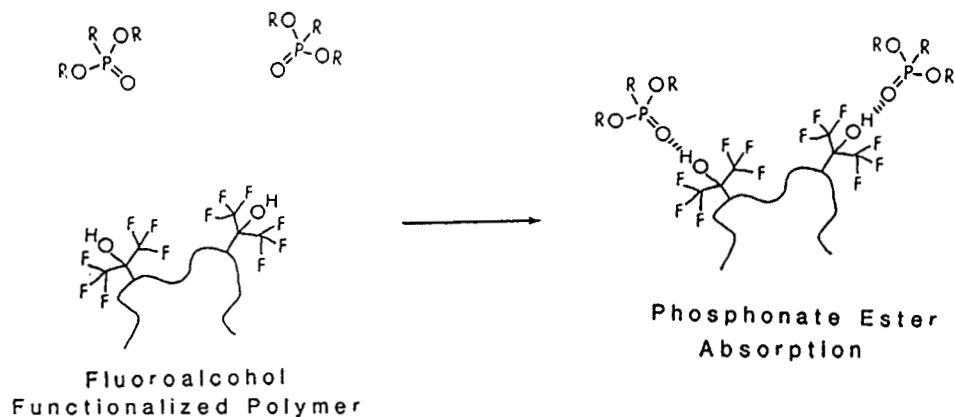
In this work, a fluoroalcohol polymer coating-phosphonate ester vapor interaction is investigated using a surface acoustic wave (SAW) device. A con-

ceptual illustration of this coating-vapor interaction and SAW device sensor response is presented in Figure 1. The phosphonate ester vapor absorption is believed to involve a hydrogen-bonded interaction between the fluoroalcohol and phosphoryl structures and to be reversibly driven by the partial pressure of the phosphonate ester. The SAW device detects extremely small gravimetric changes (subnanogram) in a coating by a shift in resonant frequency of the piezoelectric substrate corresponding to the absorption and desorption of vapors.⁹ The objective of the present work is to make systematic variations in the structure of the fluoroalcohol polymer coating and examine the corresponding variation in phosphonate ester vapor sensitivity. The structures of the fluoroalcohol functionalized and control polymers of this study are presented in Figure 2.

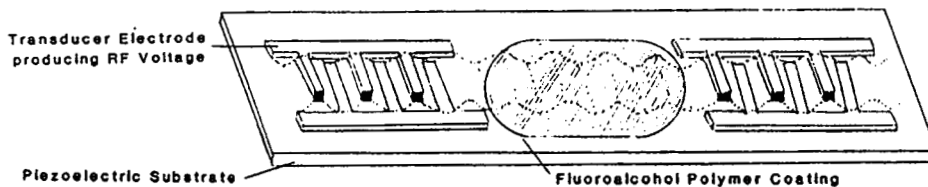
The interest in phosphonate ester vapor detection is derived from a need to detect certain toxic phosphorous compounds that behave as anticholinesterase agents such as isopropyl methylphosphonofluoridate (GB, sarin), and diisopropyl phosphorofluoridate (DFP).¹⁰ These compounds usually have a labile substituent bonded to the phosphoryl group (e.g., fluoride) that is moderately resistant to hydrolysis but is rapidly displaced during phosphorylation and inhibition of an enzyme. For routine

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Coating - Vapor Interaction



Resonating Surface Acoustic Wave Device



Sensor Response

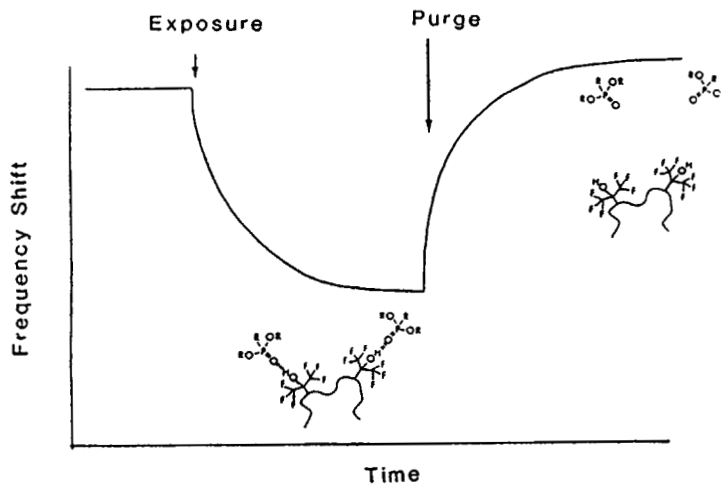


Figure 1 Schematic illustration of fluoroalcohol polymer coating-phosphonate ester vapor interaction, SAW device with interdigital electrodes generating a resonating surface acoustic wave (not to scale and highly exaggerated), and frequency response to vapor exposure.

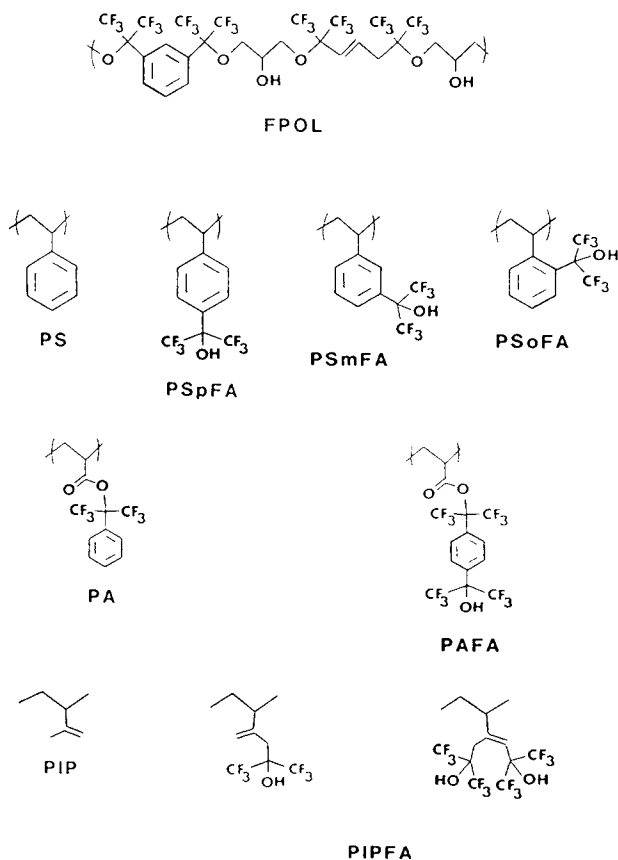


Figure 2 Structures of fluoroalcohol polymers. The two structures designated PIPFA represent the mono and diadduct of hexafluoroacetone and poly(3,4-isoprene).

study, a simulant without the labile substituent is used. Dimethyl methylphosphonate (DMMP) is the most common example.¹¹ Regarding the hydrogen-bond interaction, the hydrogen-bond acceptor strength of the phosphoryl group is only slightly changed when an adjacent fluoride is replaced by the methoxy substituent as demonstrated by the corresponding β -scale basicity values for GB ($\beta = 0.61$), DFP ($\beta = 0.63$), and DMMP ($\beta = 0.73$).¹²

The fluorine in the fluoroalcohol polymer coatings is perceived to serve two purposes: Where the hydroxyl group has two adjacent trifluoromethyl groups, they will inductively promote the hydroxyl acidity to enhance hydrogen bonding and sterically deter some of the intramolecular bonding. The fluorine presence also makes the coating hydrophobic, which significantly reduces the coating's sensitivity to water vapor as an interference.¹³

In Figure 2, with the exception of fluoropolyol (FPOL), all the fluoroalcohol polymers incorporate the hexafluorodimethylcarbinol functionality that is derived from hexafluoroacetone. The hexafluorodi-

methylcarbinol functionality was first incorporated into styrene copolymers by Pearce and co-workers to utilize the hydrogen-bonding capability for preparation of polymer blends.¹⁴ Barlow et al. extended this concept to microsensor coatings using a series of styrene-hexafluorodimethyl-4-styrylcarbinol copolymers on a piezoelectric crystal for study of DMMP absorption.^{15a} Based on Flory-Huggins chi measurements using a model compound system, they speculated that higher sensitivities might be achieved by modification of the polymer backbone structure as opposed to a higher degree of fluoroalcohol functionalization. At the time of Barlow et al.'s initial report in 1984,^{15b} we tested a fluoroepoxy prepolymer (FPOL) that was available from previous aircraft coating work.¹⁶ Although this material does not have trifluoromethyl groups positioned alpha to the hydroxyl sites, it possesses exceptional phosphonate ester sensitivity and good coating mechanical properties as a SAW microsensor coating.¹³ The remaining polymers depicted in Figure 2 were synthesized and investigated for DMMP vapor absorption to provide a structure-property data base.

EXPERIMENTAL

All reagents and solvents were of reagent-grade quality, purchased commercially, and used without further purification unless otherwise noted. Boiling points were determined during fractional distillation and are uncorrected. NMR spectra were recorded on a Varian EM-390 spectrometer with ¹H-NMR spectra referenced against tetramethylsilane and ¹⁹F-NMR spectra referenced against CFCl₃. FTIR spectra were recorded on a Perkin-Elmer 1800 spectrometer from neat thin film samples supported on or between NaCl discs. Mass spectral data were recorded on a CVC instrument at 70 eV. Glass transition temperatures were determined by differential scanning calorimetry with a DuPont 2100 Thermal Analysis System and 910 differential scanning calorimeter (5–10 mg samples, 10°C/min, nitrogen atmosphere). Polymer densities were measured by suspending several void-free granules of polymer in an aqueous sodium iodide solution, adjusting the NaI concentration until the solution density matched that of the polymer and measuring the solution density. Elemental analysis was performed by the Schwartzkopf Microanalytical Laboratory.

DMMP absorption isotherms were determined by frequency-response measurements of 158 MHz SAW devices (Microsensor Systems, part number SD-158-A) coated with a 250 KHz fluoroalcohol

polymer film exposed to varying concentrations of DMMP vapor by procedures similar to those reported elsewhere.¹⁷ Measurements were conducted at Microsensor Systems using a VG 7000 automated vapor delivery system with DMMP bubbler maintained at 15°C and SAW device at 25°C. All coatings were deposited using a spray deposition technique. A dilute solution (typically 0.2% by weight) of each polymer was prepared in chloroform or methanol and sprayed through a fine nozzle and mask onto the SAW device while it was powered and oscillating in an RF oscillator circuit (Microsensor Systems, part no. CEM-158). Clean 20 psi air was used as a spray propellant. Film thicknesses were gauged by the SAW oscillator frequency shift (in KHz) that they produced during the spray deposition process. The SAW resonant frequency was monitored using a multichannel digital frequency counter with 1 Hz resolution (Microsensor Systems, part no. DAS-158) interfaced to an Apple Macintosh computer. All devices were coated with films that produced a frequency shift of about 250 KHz. (Actual film thicknesses can be inferred from the theoretical SAW mass sensitivity of the 158 MHz device [i.e., 365 Hz/nanogram], the active area of the device [i.e., 0.08 cm²], and the density of the coating material.⁹) Since the SAW vapor sensitivity is directly related to the effective coating thickness, all results have been normalized to assume a coating frequency shift of 250 KHz in an attempt to allow accurate comparison of the intrinsic performance of the coating materials.

Naval Research Laboratory (NRL) Fluoropolyol (FPOL)

This material is a fluoroepoxy prepolymer synthesized from hexafluoroacetone, benzene, propene, and epichlorohydrin some years ago at NRL for coating applications.¹⁶

Poly([4-(1,1,1,3,3,3,-hexafluoro-2-hydroxyprop-2-yl)phenyl]ethylene) (PSPFA)

The corresponding monomer was synthesized by the Grignard reaction between the substituted styrene and hexafluoroacetone as follows: The reaction flasks and other equipment were dried at 130°C overnight and assembled under dry nitrogen. THF was distilled from sodium metal immediately before use. Initiation of the Grignard reagent was accomplished with 4-bromostyrene because much difficulty was experienced when starting with 4-chlorostyrene. 4-Bromostyrene (2.0 g, 0.011 mol) was added to a

stirred slurry of Mg (1.0 g, 0.04 mol) in 2 mL of THF. The reaction mixture exothermed and developed a green color as the Grignard reagent formed. On cooling, additional Mg (5.0 g, 0.21 mol) in 10 mL THF was added followed by dropwise addition of 4-chlorostyrene (33.1 g, 0.239 mol) dissolved in 25 mL THF. An additional 20–25 mL THF was added directly to the reaction mixture when it began to become warm. After the addition was complete (0.75 h), the dark green solution was stirred 1 h at room temperature. Hexafluoroacetone (42.8 g, 0.258 mol) was added via a gas inlet tube at 23°C, and the mixture was stirred for 1 h. The mixture was then poured into 100 mL 3N HCl, the upper yellow oil phase was separated, and the aqueous phase was extracted with 50 mL CHCl₃, which was combined with the oil phase. Volatile solvents were removed by rotary evaporation, and the product was poured into 200 mL of 10% NaOH solution. This NaOH solution was rotary evaporated over a warm water bath for 6 min, then diluted with 200 mL of 6N HCl. The yellow oil and three 60 mL CHCl₃ extracts were combined, dried over sodium sulfate, filtered, and concentrated by rotary evaporation to yield a product that contained 9% THF (GC analysis) that could not be removed by further distillation. The THF was separated by redissolution in 250 mL 10% NaOH, continuous warm rotary evaporation, addition to 200 mL 3N HCl, combination of the oil phase and one 100 mL CHCl₃ extract, redrying, and vacuum distillation to yield 39.9 g (59%, 99% GC purity) of monomer: bp 61–63°C/3 Torr; d_{20}^{20} 1.374; n_D^{24} 1.4530; ¹H-NMR (CDCl₃) 4.1 (s, 1H, –OH), 5.7 (d, 1H, *cis* HC=CHPh) $J_{H,H}$ = 11 Hz, 6.4 (d, 1H, *trans* HC=CHPh) $J_{H,H}$ = 17 Hz, 7.1 (dd, ¹H, =CHPh) $J_{H,H}$ = 11 and 17 Hz, 8.0 (AABB, 4H, C₆H₄); ¹⁹F-NMR (CDCl₃) –76.5 (s); IR (neat) 3605, 3545, 3093, 3052, 3017, 1634, 1613, 1516, 1411, 1365, 1328, 1268, 1212, 1207, 1202, 1166, 1106, 1034, 1019, 989, 972, 950, 923, 841, 748, 717 cm⁻¹; MS (M/Z) 270 (34%, M⁺), 201 (70%, M–CF₃), 131 (100%, CH₂=CHC₆H₅CO⁺); UV (CH₃OH) 290 nm (ϵ = 1430), 280 (ϵ = 2130), 243 (ϵ = 25,900).

The polymerization was conducted as follows: Into a Carius tube were weighed monomer (5.01 g, 19 mmol), AIBN (0.131 g, 0.80 mmol), and 12.5 mL of benzene. The contents degassed with three freeze–evacuate–thaw cycles, sealed, and polymerized at 60°C for 20 h. The polymer was worked up by three reprecipitations from CHCl₃ into petroleum ether followed by vacuum drying (50°C/1.5 h) to yield 4.08 g (80%): ¹H-NMR (acetone-*d*₆) 0.67 to 1.33 (broad signal, –CH₂–), 3.97 (broad signal, 1H, –CHPh–), 6.03 (broad signal, 2H), 7.00 (broad

signal, 2H); ^{19}F -NMR (acetone- d_6) -75.0 (broad signal); IR (neat) 3600, 3504, 2925, 2850, 1614, 1513, 1368, 1270, 1217, 1168, 1101, 970, 949, 926, 832, 740, 709 cm^{-1} ; UV (CH_3OH) 257, 252 nm.

Poly([3-(1,1,1,3,3,3-hexafluoro-2-hydroxyprop-2-yl)phenyl]ethylene) (PSmFA)

The corresponding monomer was synthesized from 3-bromostyrene (5.11 g, 0.028 mol), Mg (0.7 g, 0.029 mol), 30 mL of THF and hexafluoroacetone (4.3 g, 0.026 mol) by a procedure analogous to that for PSpFA and yielded 3.90 g (52%): bp 40–43°C/0.1 Torr; d^{20} 1.364, n_D^{24} 1.4488; ^1H -NMR (CDCl_3) 4.1 (s, 1H, $-\text{OH}$), 5.3 (d, 1H) $J_{\text{H,H}} = 11$ Hz, 5.8 (d, 1H) $J_{\text{H,H}} = 18$ Hz, 6.8 (dd, 1H), 7.3–7.8 (m, 4H); ^{19}F -NMR (CDCl_3) -75.3 (s); IR (neat) 3604, 3542, 3209, 3094, 2986, 2884, 1634, 1605, 1584, 1488, 1440, 1406, 1367, 1288, 1267, 1208, 1154, 1126, 1090, 1055, 1001, 989, 970, 916, 802, 749, 725, 711, 665 cm^{-1} .

Polymerization, analogous to the procedure for PSpFA, involved monomer (3.44 g, 0.013 mol) initiated by AIBN (0.011 g, 0.0008 mol) in 10 mL of benzene at 60°C to yield 2.23 g (65%) polymer. ^1H -NMR (acetone- d_6) 0.30 to 1.30 (broad signal), 2.58 (s, 1H), 5.9 (broad signal, 1H) 6.5 (broad signal, 2H), 6.7 (broad signal, 1H); ^{19}F -NMR (acetone- d_6) -75.7 (bs); IR (neat) 3605, 3520, 3045, 2929, 2853, 1608, 1490, 1444, 1365, 1268, 1208, 1151, 1124, 1088, 970, 901, 796, 743, 722, 702 cm^{-1} .

Poly[2-(1,1,1,3,3,3-hexafluoro-2-hydroxyprop-2-yl)phenyl]ethylene) (PSoFA)

The corresponding monomer was synthesized from 2-bromostyrene (1.55 g, 9.0 mmol); Mg (0.22 g, 1.0 mmol), 8.5 mL of THF, and hexafluoroacetone (3.0 g, 18 mmol) by a procedure analogous to that for PSpFA and yielded 0.99 g (43%): bp 35–37°C/0.1 Torr; n_D^{24} 1.4492; ^1H -NMR (CDCl_3) 4.32 (s, 1H, $-\text{OH}$), 5.45 (dd, 1H, $-\text{OH}$), 5.45 (dd, 1H) $J_{\text{H,H}} = 10.8$ and 1.5 Hz, 5.52 (dd, 1H) $J_{\text{H,H}} = 17.6$ and 1.5 Hz, 7.33 to 7.78 (m, 5H); ^{19}F -NMR (CDCl_3) -74.2 (s); IR (neat) 3588, 3526, 3091, 3074, 2990, 2884, 1626, 1571, 1489, 1446, 1412, 1366, 1301, 1258, 1224, 1203, 1177, 1151, 1110, 1060, 1030, 995, 965, 951, 927, 841, 785, 767, 749, 713, 662 cm^{-1} .

Polymerization, analogous to the procedure for PSpFA, involved monomer (0.96 g, 4.0 mmol) initiated by AIBN (0.0032 g, 0.3 mmol) in 3 mL of benzene at 60°C to yield 0.24 g (25%) polymer, ^{19}F -NMR (acetone- d_6) -75 (s); IR (neat) 3590, 3350, 3065, 3033, 2964, 2933, 1607, 1581, 1487, 1455, 1255, 1229, 1212, 1174, 1117, 965, 948, 924, 755, 711 cm^{-1} .

Poly[(phenyl-1,1,1,3,3,3-hexafluoropropylidene) oxycarbonylethylene] (FA)

The corresponding monomer was prepared by reacting 2-hydroxy-2-phenyl-1,1,1,3,3,3-hexafluoropropane (61.0 g, 0.250 mol) with acryloyl chloride (27.15 g, 0.300 mol, dropwise addition 1.25 h) catalyzed by triethylamine (30.36 g, 0.300 mol) in 100 mL Freon 113 at 5–15°C for 1.5 h. After aqueous acid (100 mL 1.5N HCl) and base (2 × 100 mL 1.0N NaOH) extraction and drying (saturated NaCl extraction), the monomer was isolated by fractional vacuum distillation (50–57°C/0.2 Torr) followed by alumina column chromatography (Freon 113 elution) to yield 34.8 g (47%) of 99.8% (GC) pure monomer: bp 55–57°C (0.2 Torr); $n_D^{24} = 1.4350$.

A 1.15 g quantity of this monomer was polymerized with 0.0024 g AIBN in 8 mL THF at 60°C. The polymer was isolated by precipitation in 500 mL 60/40 methanol/water and vacuum dried. IR (neat) 3071 2961, 2879, 1782, 1502, 1454, 1273, 1250, 1225, 1197, 1152, 1113, 1092, 1065, 1037, 993, 950, 758, 716, 703 cm^{-1} .

Poly([4-(1,1,1,3,3,3-hexafluoro-2-hydroxyprop-2-yl)phenylene-1,1,1,3,3,3-hexafluoropropylidene] oxycarbonylethylene) (PAFA)

The corresponding monomer was prepared by reaction of 1,4-bis(2-hydroxyhexafluoro-2-propyl) benzene (5.00 g, 0.012 mol) with acryloyl chloride (0.99 g, 0.011 mol, dropwise addition 45 min) catalyzed by triethylamine (3.70 g, 0.036 mol) in 120 mL diethyl ether at 2–4°C for 1.33 h. After aqueous acid (2 × 50 mL 3N HCl) and base (2 × 30 mL 1M NaHCO_3) extraction and drying (saturated NaCl extraction), the product was analyzed by GC to contain 45.2% diol, 37.7% monoacrylate, and 19.9% diacrylate. The diol was separated by vacuum sublimation (60°C/0.15 Torr). The diacrylate and monoacrylate were separated by silica column chromatography with chloroform elution followed by vacuum sublimation (90°C/0.1 Torr) of the monoacrylate-containing fractions. A second silica column and sublimation purification cycle yielded monoacrylate monomer > 99% pure by GC. Yield 1.03 g (18%); mp 112–113.5°C; ^1H -NMR (CHCl_3) 3.60 (s, 1H, $-\text{OH}$), 6.05–6.80 (m, 3H, $\text{CH}_2=\text{CH}-$), 7.54–7.80 (AA'XX', 4H, aromatic); ^{19}F -NMR, -70.5 (s, CF_3 adj to acrylate), -76.5 (s, CF_3 adj to hydroxyl).

This monoacrylate monomer (0.28 g, 0.60 mmol) was polymerized using AIBN (0.00048 g, 0.0029

mmol) initiator in 2 mL THF at 60°C. The polymer was isolated by precipitation in water and vacuum dried with periodic warming to 60°C. Yield 0.1558 g (56%), IR (neat) 3607, 3486, 2961, 2885, 1774, 1518, 1424, 1378, 1269, 1230, 1202, 1157, 1118, 1074, 1027, 995, 974, 956, 930, 826, 750, 716 cm^{-1} .

Poly(3,4-isoprene) functionalized fluoroalcohols, PIPFA1 and PIPFA2

The precursor polymer, poly(3,4-isoprene), was prepared by Ziegler–Natta polymerization using a modified procedure of Natta et al.¹⁸ The catalyst was prepared by inert atmosphere addition of 0.25 mL titanium tetrapropoxide followed by 0.75 mL triethylaluminum to 50 mL dry toluene. After aging for 15 min, 15 mL freshly distilled isoprene was added and the polymerization conducted at 23°C for 10 h. The polymer was isolated by precipitation into 300 mL methanol acidified with 0.5 mL of concentrated HCl and vacuum dried to yield 1.32 g (13%).

PIPFA1 was prepared by reacting 0.50 g PIP with 7.73 g hexafluoroacetone in 3 mL benzene in a small Fisher–Porter tube at 120°C for 12 h. On cooling, the polymer precipitated from solution and was purified by dissolution in methanol and precipitation in diethyl ether followed by vacuum drying to yield 0.93 g. In contrast to the transparent rubbery PIP precursor, this product had a fine fibular and an opaque white character. Film cast from methanol had to be very thin to achieve moderate transparency.

Elemental ANAL: Found: C, 44.32; H, 3.93; Calcd for $\text{C}_5\text{H}_8(\text{C}_3\text{F}_6\text{O})_{0.80}$: C, 44.22; H, 3.98. IR (neat) 3590, 3440, 2940, 2863, 1451, 1256, 1213, 1147, 1013, 967, 925, 733, 712, 685 cm^{-1} .

PIPFA2 was prepared by reacting 0.25 g PIP with 0.36 g hexafluoroacetone in 3 mL of benzene in a small Fisher–Porter tube at 100°C for 12 h. The reaction mixture was evaporated to dryness, the product dissolved in methanol, precipitated into water, and vacuum dried to yield 0.39 g. This product was transparent and glassy in character.

ANAL: Found: C, 53.45; H, 5.48; Calcd for $\text{C}_5\text{H}_8(\text{C}_3\text{F}_6\text{O})_{0.46}$: C, 53.04; H, 5.54. IR 3593, 3459, 3076, 2966, 2936, 2870, 1644, 1447, 1378, 1207, 1142, 1016, 993, 966, 895, 734, 711, 682 cm^{-1} .

Acylation of FPOL and PSpFA

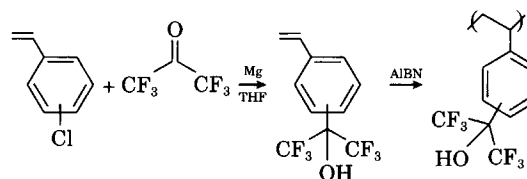
A 0.65 g quantity of FPOL was reacted with 0.57 g acetyl chloride catalyzed by 0.73 g triethylamine in

10 mL chloroform at 20°C for 1 h. The reaction mixture was extracted with 5% HCl and water, dried over Na_2SO_4 , filtered, evaporated to dryness, and vacuum dried to yield 0.67 g. A 0.32 g quantity of PSpFA was reacted with 0.47 g acetyl chloride catalyzed by 0.60 g triethylamine in 10 mL of THF at 20°C for 3 h. The reaction was worked up as above for the FPOL acylation. An IR spectrum indicated only a partial acylation had been accomplished, and the product was cycled through the acylation reaction two more times to yield 0.22 g product with a 90% acylation based on the decreased hydroxyl band intensity.

RESULTS AND DISCUSSION

Synthesis

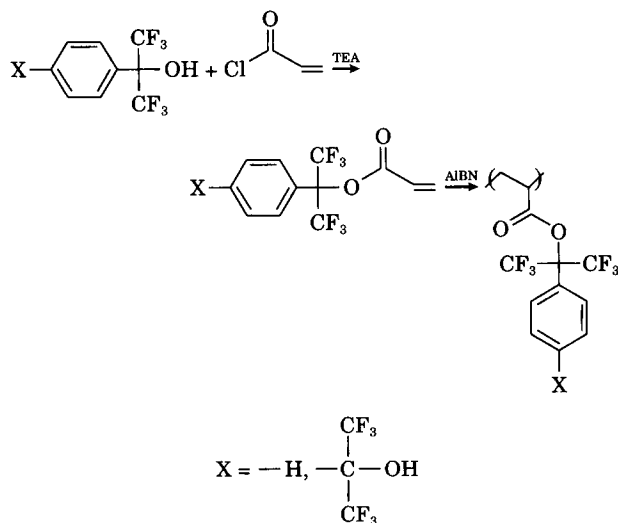
The *ortho*-, *meta*-, and *para*-hexafluorodimethylcarbinol-substituted polystyrenes (PSoFA, PSmFA, and PSpFA, respectively) were synthesized to investigate the positional isomer effect. PSpFA was prepared from the monomer that was synthesized from *p*-chlorostyrene by a method similar to that reported by Pearce et al.¹⁹ PSmFA and PSoFA were analogously prepared by reaction of the corresponding Grignard reagents and hexafluoroacetone followed by free radical polymerization as follows:



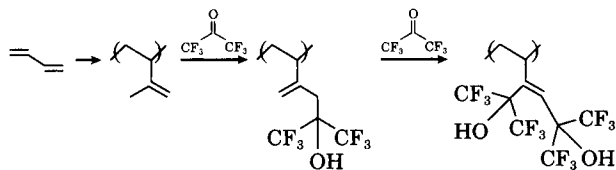
Initially, there was some concern that the tertiary hydroxyl would adversely affect the polymerization by way of chain transfer, but a control styrene polymerization in the presence of the model compound, hexafluorodimethylphenylcarbinol, demonstrated that the hydroxyl had a negligible effect on the molecular weight and yield of polystyrene. However, the *ortho*-substituted styrene monomer polymerized poorly and only a trivial amount was available for study. Considering the size of the hexafluorodimethylcarbinol group, it appears that a steric effect may be suppressing the polymerization.

A polyacrylate fluoroalcohol (PAFA) and polyacrylate control (PA) were synthesized as comparative analogs with the polystyrene series. The issue of interest here is the effect of a basic ester group incorporated into the polymer structure. PA and PAFA were synthesized according to the following reactions. The monomer corresponding to PAFA

involved a careful chromatographic separation from the monoacrylate–diacrylate–diol product mixture:



A third approach is directed at incorporation of the hexafluorodimethylcarbinol group into an isoprene rubber that complements previous observations that rubbery coatings have higher absorption capacity for vapors.¹ The poly(3,4-isoprene-fluoroalcohols) (PIPFA1 and PIPFA2) were synthesized by reacting poly(3,4-isoprene) with hexafluoroacetone, presuming similar chemistry to occur as reported by Urry et al. for the reaction of perfluoroketones with terminal olefins.²⁰ Multiple addition of hexafluoroacetone to the 3,4-isoprene repeat unit is possible:



Two polymers were prepared: one with a high ratio of hexafluoroacetone-to-isoprene repeat unit (PIPFA1, 80% of repeat units functionalized as determined by elemental analysis) and one with a low ratio (PIPFA2, 46% of repeat units functionalized as determined by elemental analysis). The IR spectra (see Fig. 4) reflect this difference in the ratio of OH-to-CH band intensities. From the degree of functionalization analysis, it appears that very little double addition to a single isoprene repeat unit occurred. However, this functionalization dramatically alters the morphological character of the polymer. The initial poly(3,4-isoprene) is a rubber, whereas PIPFA2 is glassy and PIPFA1 is fibrous and opaque. In the DSC thermogram, PIPFA1 displays an en-

dotharm peak at 60°C rather than a slope change corresponding to a glass transition temperature. Similar behavior has been reported for trifluoromethyl vinyl acetate copolymers but is not understood.²¹

In addition to the monomer and polymer characterization data in the experimental section, density and glass transition temperature data on the fluoroalcohol and control polymer coatings are listed in Table I. The density roughly follows the fluorine content of the polymer. Within the polystyrene series, substitution at the *meta* position compared with the *para* position results in a lower T_g and slightly lower density. The lower symmetry of the *meta* substitution may have the effect of reducing packing efficiency or increasing free volume, which could account for glass transition and density effects relative to the *para* substitution. In the polyacrylate (PAFA and PA) and polyisoprene (PIPFA1, PIPFA2, and PIP) series, the hexafluorodimethylcarbinol substituent raises both the T_g and density as would be expected from the effect of hydrogen bonding and steric bulk. In the fifth column of Table I, the hydroxyl molar equivalent concentration is presented as calculated from the density, repeat unit molecular weight, and repeat unit hydroxyl functionality. This parameter will allow correlation of the hydroxyl group concentration in the coating with the DMMP vapor absorption response.

SAW Results

As schematically illustrated in Figure 1, SAW devices were coated with thin films of the fluoroalcohol polymers and used as a sensor for the absorption and desorption of DMMP vapor. SAW chemical sensors use a delay line configuration that consists of a set of lithographically patterned interdigital electrodes (IDTs) deposited onto the surface of an optically smooth piezoelectric substrate. When a time-varying potential is applied to the “transmitting” IDT, a Rayleigh surface wave is created and propagates across along the device surface. This surface wave is converted back into an electrical signal by the “receiving” IDT. When a SAW delay line is used as the feedback element in an oscillator circuit, the frequency of the circuit is linearly related to the surface wave velocity. The SAW velocity is strongly perturbed by surface mass loading. Applying a polymeric coating to the SAW device will shift the resonant frequency of the SAW oscillator by an amount related to the mass per unit area applied to the device. When vapors absorb into the coating, there is a further incremental change in the mass loading experienced by the SAW device. It is this

Table I Glass Transition Temperature, Density Fluorine Content, and Hydroxyl Molar Equivalent Concentration Data for Fluoroalcohol Polymer Coatings, and Their 158 MHz SAW Response (25°C) to DMMP Vapor at P/P_0 (15°C) = 0.032

Coating	T_g (°C)	d^{20} (g/cm ³)	%F	[OH]	Δf (KHz) at $P/P_0 =$ 0.032
FPOL	10	1.607	51.0	3.59	14
PSpFA	122	1.444	42.2	5.35	39
PSmFA	84	1.433	42.2	5.31	45
PS	105	1.047	—	—	0.5
PAFA	175	1.491	49.1	3.21	42
PA	96	1.456	38.3	—	1.3
PIPFA1	60	1.397	45.4	5.57	51
PIPFA2	32	1.294	36.3	4.13	34
PIP	-22	0.902	—	—	3.0

incremental change in mass of the coating caused by exposure to chemical vapors that makes chemical sensing with SAW devices possible.

DMMP vapor absorption isotherms were determined by depositing a thin film of polymer on a 158 MHz SAW device and measuring the frequency shift with varying DMMP vapor concentration exposure up to 40% saturation at 25°C. These data for the polystyrene, polyacrylate, and polyisoprene fluoroalcohol series are presented in Figure 3. The fluoroalcohol substitution causes the DMMP vapor absorption isotherm to rise very steeply at the low concentration end and to level off toward saturation at the high concentration end. The PS and PA control polymers display only a nominal or very slowly increasing absorption of DMMP with pressure and very little sensitivity at the low concentration end of the isotherm. As a relative measure of DMMP vapor sensitivity, the frequency response values at the low concentration end of the isotherm ($P/P_0 = 0.032$) have been entered in column 6 of Table I. A general detection limit of 0.03 ppm can be estimated using a 40 KHz response and a P_0 value of 0.80 Torr (DMMP vapor pressure from the source bubbler at 25°C) and assuming a linear isotherm below the 0.032 value and a frequency resolution of 10 Hz with a signal-to-noise ratio of 3.

The SAW frequency shift response may also be expressed as a weight percent of absorbed DMMP by dividing it by the 250 KHz frequency shift caused by the coating deposition. Typically, for strong 100 KHz DMMP shifts, the corresponding weight percent of absorbed DMMP is 40%. The large enhancement resulting from incorporating the hexafluorodimethylcarbinol group in the polymer matrices is observed by comparison of the PS, PA, and

PIP controls with the corresponding fluoroalcohol polymers. The quantity of DMMP absorbed might be expected to correlate with the concentration of hydroxyl groups in the film. Comparing the values of coating hydroxyl concentrations in the polystyrene, polyacrylate, and polyisoprene coatings (Table I, column 5) with the relative amount of DMMP absorbed (Fig. 3 and Table I, column 6), this trend appears to be generally followed although PAFA is a noticeable outlier. It is possible to calculate a frequency shift at which there would be stoichiometric equivalence between the DMMP phosphoryl and coating hydroxyl groups. These values for the corresponding coatings are PSpFA and PSmFA (115 KHz); PAFA (67 KHz); PIPFA1 (160 KHz); PIPFA2 (99 KHz); and FPOL (69 KHz). If stoichiometric hydrogen-bonded complexes were exclusively being formed, greater discrimination between coatings would be expected. An interpretation of the coating response data cannot be based on hydroxyl site concentration alone, and other factors need to be considered such as degree of intramolecular hydrogen bonding in the coating, strength of the hydrogen bond, coating morphology, and nonhydrogen-bonded interactions.

For the polystyrene series, the order of DMMP vapor sensitivity dependence on fluoroalcohol isomer substitution is *meta* > *para* > *ortho*. In the hydroxyl region of the infrared spectrum, this order is paralleled by the intensity of the free hydroxyl band at 3600 cm⁻¹ relative to that of the hydrogen-bonded hydroxyl at 3400–3500 cm⁻¹ (Fig. 4). The intensity of the free hydroxyl band of PSpFA is exceptionally small and appears to indicate from inspection of the structure (Fig. 2) that a neighboring group intramolecular hydrogen bonding is occurring. The free

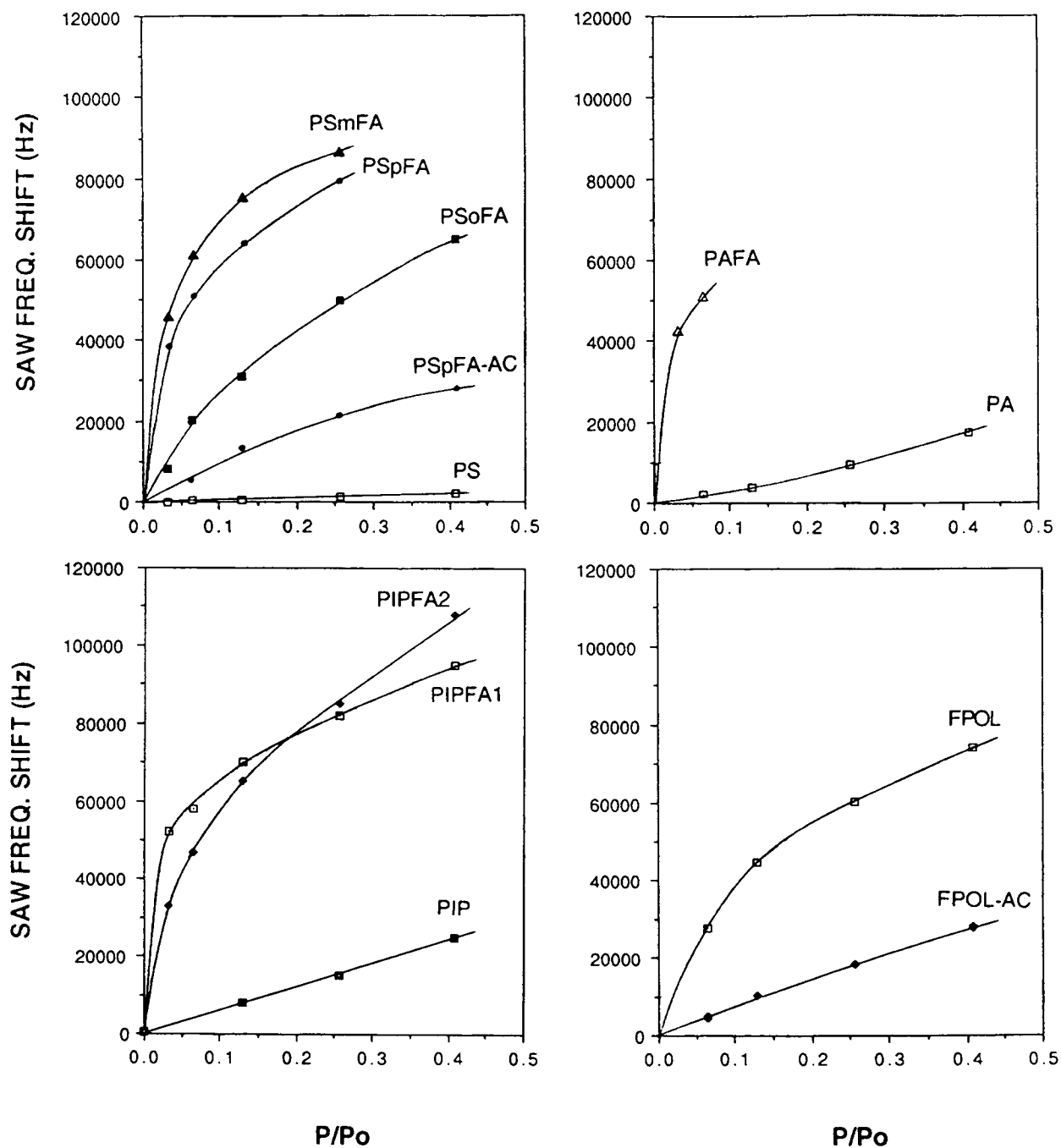
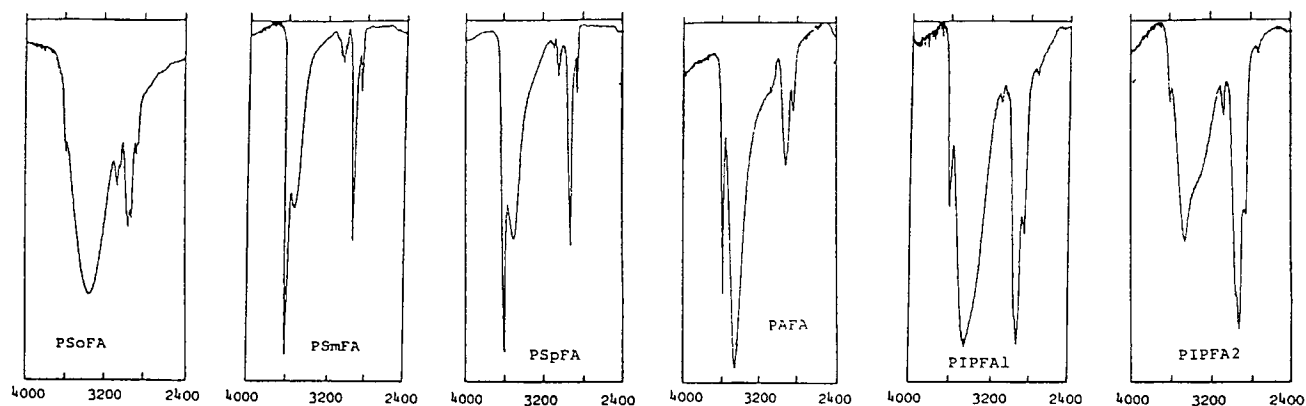


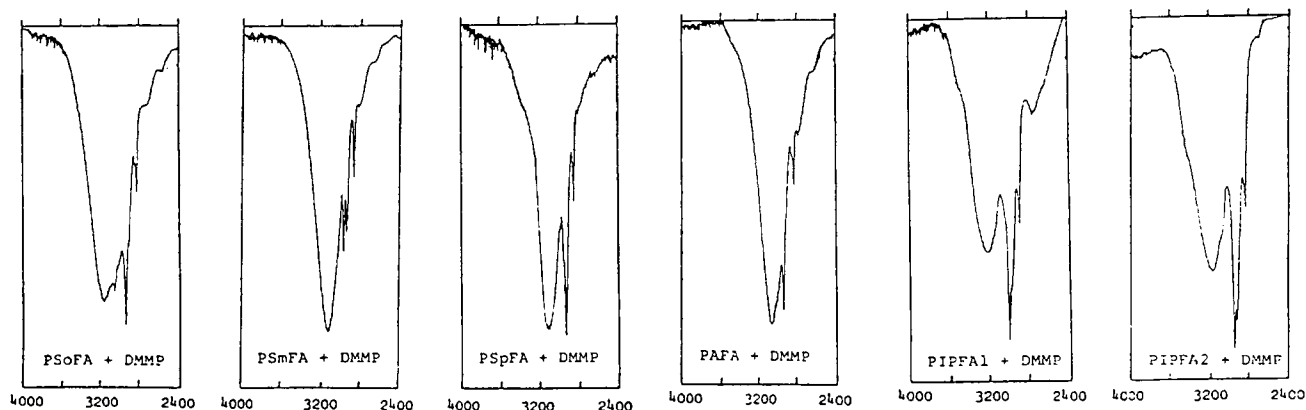
Figure 3 Frequency response measurement (158 MHz SAW device) of DMMP vapor absorption isotherm at 25°C for fluoroalcohol polymer coatings (structures and compositions are presented in Fig. 2 and in the Experimental section).

hydroxyl band intensity of PSmFA is slightly greater than that of PSpFA, and this observation is consistent with the symmetry-induced free volume effect that was related to the density and T_g differences of these two polymers. Within the polystyrene series, this correlation of free hydroxyl content with DMMP vapor absorption sensitivity could be inter-

preted that the free hydroxyl is a stronger DMMP receptor site than is the hydrogen-bonded hydroxyl. However, this interpretation cannot solely be used to account for the comparison between the polystyrene and polyacrylate or polyisoprene fluoroalcohol series that have similar DMMP vapor responses but smaller free hydroxyl contents. Other factors such



Hydroxyl Region Infrared Spectra of Fluoroalcohol Polymers



Same Spectra after DMMP Vapor Absorption

Figure 4 Infrared spectra of fluoroalcohol polymer hydroxyl region before and after DMMP vapor absorption.

as nature of the unfunctionalized matrix and hydroxyl group concentration are also issues in such comparisons. For example, comparison of the DMMP absorption isotherms for the control polyacrylate (PA) and control polystyrene (PS) indicates that DMMP is more strongly absorbed into the polyacrylate matrix. Addition of the hexafluorodimethylcarbinol functionality to these matrices then results in a proportionately larger enhancement to the polystyrene matrix. It is then not clear whether to attribute this enhancement to the higher free hydroxyl content (Fig. 4) or to the higher hydroxyl concentration (Table I). Both favor this effect.

The polyisoprene series differs from the polystyrene and polyacrylate homopolymer series in that the degree of hexafluorodimethylcarbinol function-

alization is varied in an initially nonglassy matrix. At low DMMP vapor concentrations, the more highly functionalized PIPFA1 displays the stronger absorption and is the more sensitive coating (Fig. 3). A similar trend was reported in Barlow's study of styrene-hexafluorodimethyl-4-styrylcarbinol copolymers.¹⁵ At higher DMMP concentrations, there is an isotherm crossover and PIPFA2 becomes the stronger absorbent. This effect may be related to the more rubbery character of PIPFA2.

IR Observations of Hydrogen Bonding

The hydrogen-bond formation that accompanies the absorption of DMMP in the fluoroalcohol polymers is clearly evident from comparison of the hydroxyl region of the infrared spectra of polymer films before

Table II Infrared Hydroxyl Absorption Frequencies of Fluoroalcohol Polymer Coatings and Their Response to Absorption of DMMP Vapor

Coating	PSoFA	PSmFA	PSpFA	PAFA	PIPFA1	PIPFA2	FPOL
ν_{OH} (free)	3590	3605	3600	3607	3590	3593	3601
ν_{OH} (DMMP)	3175	3110	3118	3088	3166	3176	3370

and after DMMP vapor exposure (Fig. 4). The wavenumbers of the free hydroxyl and shift after DMMP absorption are presented in Table II. The magnitude of the shift relates to the strength of the hydrogen bond and has been correlated with the

bonding enthalpy for a hexafluoroisopropanol model compound²² and for a modified polystyrene analog.²³ Hexafluoroisopropanol forms a nonisolatable hydrogen-bonded complex with DMMP accompanied by a hydroxyl shift from 3600 to 3190 cm^{-1} in carbon

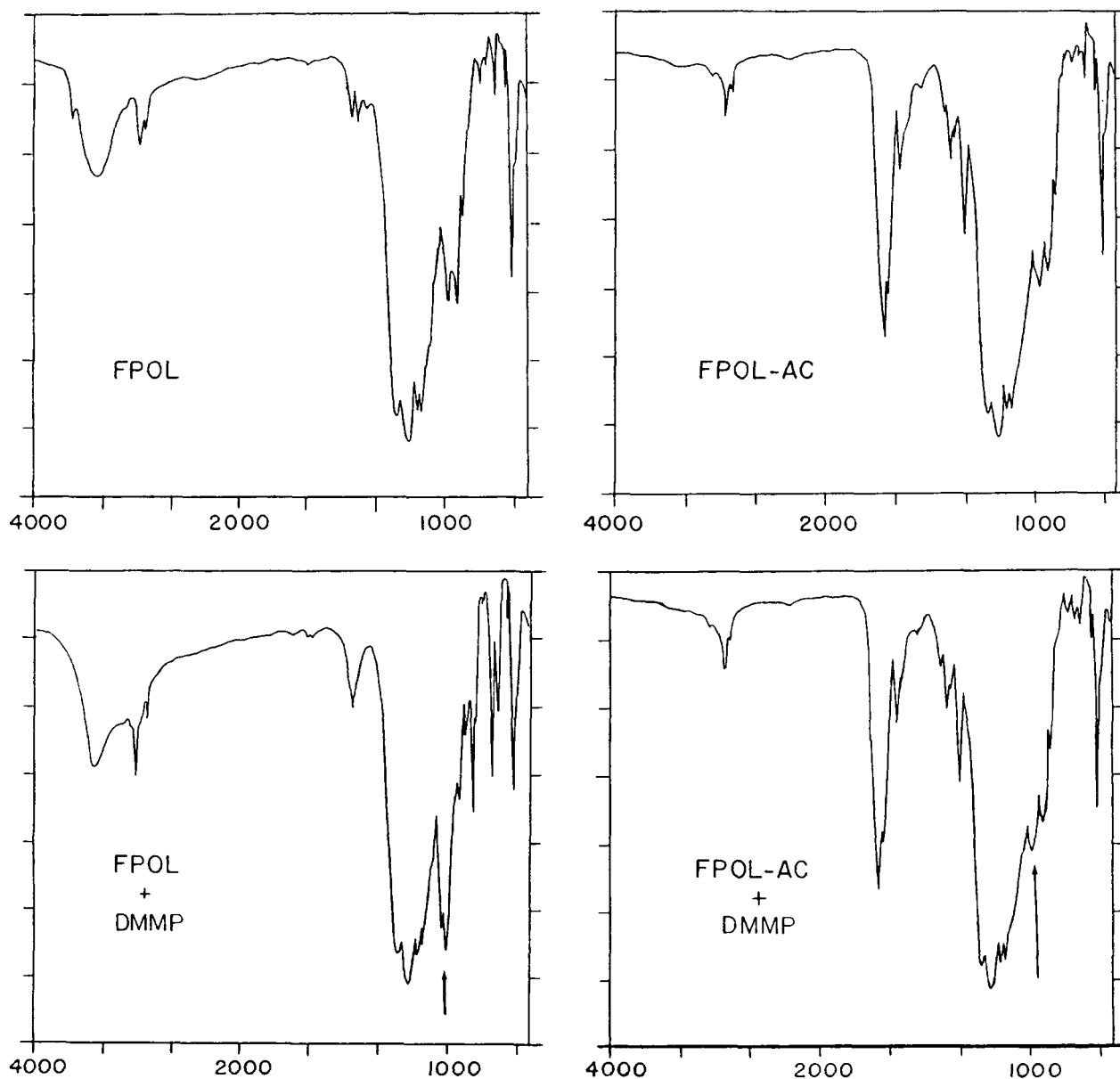


Figure 5 Infrared spectra of FPOL and its acylated analog, FPOL-AC, before and after DMMP vapor absorption. The arrows indicate the strongest DMMP band.

tetrachloride solution.¹⁵ This shift is generally followed by the fluoroalcohol polymers in Table II. Noteworthy is that PSpFA displays the largest shift that might be associated with an inductive effect from the second hexafluoroisopropyl group attached to the benzene ring.

Acylation Effect

To further illustrate the effect of the fluoroalcohol group on DMMP absorption, FPOL and PSpFA were acylated and retested for DMMP absorption.

The SAW isotherm data are presented in Figure 3. FPOL is a weaker absorbent for DMMP than is PSpFA as may be expected noting that the acidity of the FPOL hydroxyl group is weaker and its concentration is lower. The effect of converting the hydroxyl to an acetate group is a marked lowering of the DMMP absorption, particularly at the low concentration end of the isotherm as indicated by the very large difference in slopes. This is an important aspect for detection applications directed at high sensitivities. It is also noteworthy that the isotherms of these acylated analogs, FPOL-AC and PSpFA-

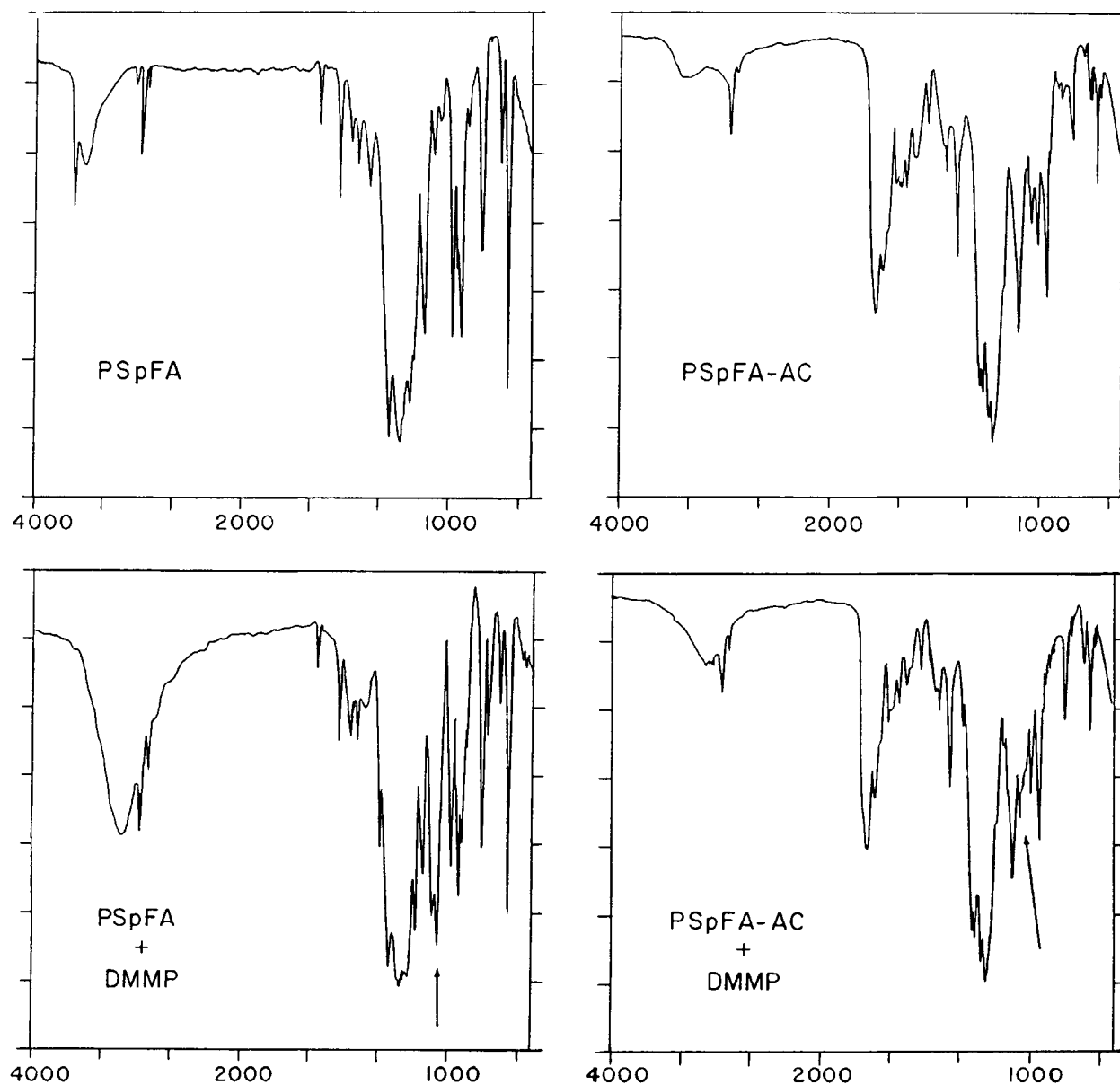


Figure 6 Infrared spectra of PSpFA and its acylated analog, PSpFA-AC, before and after DMMP vapor absorption. The arrows indicate the strongest DMMP band.

AC, are markedly similar to that of PA (Fig. 3), which is also an ester-containing matrix.

The infrared spectra of FPOL and PSpFA, their acylated analogs, and their DMMP vapor absorption provide additional molecular insight (Figs. 5 and 6). The free hydroxyl content as indicated by the relative intensity of the 3600 cm^{-1} band is substantially greater for PSpFA. However, the acylation reaction was nearly quantitative for FPOL and only approached 90% after three acylation cycles for PSPFA, as indicated by the residual hydroxyl band at 3400 cm^{-1} . The 1760 cm^{-1} carbonyl band of the acyl group is also prominent. When DMMP vapor is absorbed by FPOL and PSpFA, the free and hydrogen-bonded hydroxyl bands are shifted to the DMMP hydrogen-bond complex bands at 3370 and 3118 cm^{-1} , respectively (Table II). The smaller shift for the FPOL complex reflects the weaker hydrogen bonding of its hydroxyl group. The most prominent DMMP band is at 1040 cm^{-1} , as indicated by the arrows in Figures 5 and 6. When the acylated analogs are exposed to DMMP vapor, the absorption is much less, as is indicated by the intensity of the 1040 cm^{-1} band, which is consistent with the SAW result above.

SUMMARY

The hexafluorodimethylcarbinol group functionalized into a polymeric coating promotes a strong absorption for DMMP by a hydrogen-bonded interaction. The coating sensitivity dependence on DMMP vapor concentration is largest at the low concentration region of the absorption isotherm. This trend was common to the polystyrene, polyacrylate, and poly(3,4-isoprene) matrix structures. For the isomeric polystyrene fluoroalcohols, the order of sensitivity was *meta* > *para* >> *ortho* and was paralleled by the relative ratio of free hydroxyl to hydrogen-bonded hydroxyl content. Hydrogen bonding of absorbed DMMP resulted in a hydroxyl band shift of 400 to 500 cm^{-1} in the IR spectrum. Acylation of the fluoroalcohol group markedly reduced the DMMP sensitivity.

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