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Functionalized fluoroalkyl and alkenyl silanes: Preparations, reactions, and synthetic applications

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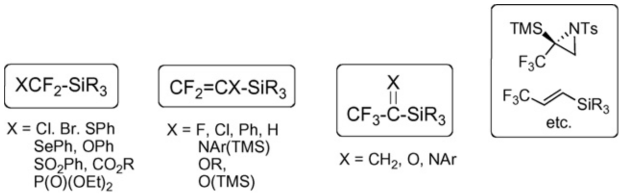

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Synthesis and properties of gemini-type hydrocarbon–fluorocarbon hybrid surfactants

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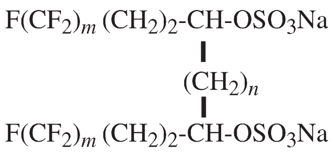

$$\begin{array}{c} F(CF_2)_m\,(CH_2)_2\text{-}CH\text{-}OSO_3Na \\ | \\ (CH_2)_n \\ | \\ F(CF_2)_m\,(CH_2)_2\text{-}CH\text{-}OSO_3Na \end{array}$$

m=4,6 n=5,6,7,8

Fm(Hn)FmOS

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Synthetic and mechanistic aspects of the reactions between bromodifluoromethyltriphenylphosphonium bromide and dibromofluoromethyltriphenylphosphonium bromide and trialkylphosphites

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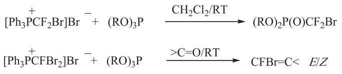

$$[Ph_3\overset{+}{P}CF_2Br]\overset{-}{Br} + (RO)_3P \xrightarrow{CH_2Cl_2/RT} (RO)_2P(O)CF_2Br$$

$$[Ph_3\overset{+}{P}CFBr_2]\overset{-}{Br} + (RO)_3P \xrightarrow{>C=O/RT} CFBr{=}C< \;\; E/Z$$

Bromofluoromethylphenylphosphonium halides react with trialkylphosphites in two distinct ways. Bromodifluoromethyltriphenylphosphonium halides undergo a rapid exchange reaction with trialkylphosphites to give the corresponding bromodifluoromethylphosphonates. A similar exchange reaction also occurred with an analogous dialkoxyphenylphosphonite. Mechanistically, the exchange process involves formation of difluorocarbene *via* dissociation of the intermediate difluoromethylene ylide, capture of the difluorocarbene by the trialkylphosphite to give , which captures bromine followed by dealkylation to produce the bromodifluoromethylphosphonate. The equilibria involved in the multi-step mechanism are all shifted to the phosphonate product by the final dealkylation step. This method provides a rapid clean entry to bromodifluoromethylphosphonates or phosphinates from a common intermediate. The yields are equal or better than the Michaelis–Arbuzov methodology [R.W. Vander Haar, D.J. Burton, D.G. Naae, J. Fluorine Chem. 1 (1971/1972) 381–383] and the reaction is especially useful for volatile phosphites due to the mild reaction conditions (RT). In contrast to the bromodifluoromethylphosphonium salt, dibromofluoromethyltriphenylphosphonium bromide does not undergo exchange reactions with trialkylphosphites. The phosphite serves as a halophilic reagent to abstract Br from the dibromofluoromethylphosphonium salt to generate the bromofluoromethylene ylide, which can easily be trapped with aldehhydes or ketones *in situ* to give *E*/*Z*-bromofluoroalkenes. This approach gives yields as good or better than those from $R_3P/CFBr_3$ or metal dehalogenation of dibromofluoromethylphosphonium salts [D.J. Burton, Z.-Y. Yang, W. Qiu, Chem. Rev. 96 (1996) 1641–1715; R.W. Vander Haar, D.J. Burton, D.G. Naae, J. Fluorine Chem. 1 (1971/1972) 381–383; R.W. Vander Haar, Ph.D. Thesis, University of Iowa, 1973]. It also avoids the formation of R_3PBr_2 as a by-product, which can react with aldehyde substrates to decrease the yield of the bromofluoroolefin. It also works well with ketones, such as $C_6H_5C(O)CF_2Cl$, which reacts readily with Zn or Zn/Cu, again lowering the yield of the olefinic product.

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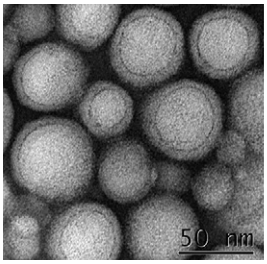
Synthesis, modification and characterization of core–shell fluoroacrylate copolymer latexes



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Two fluoroacrylate latexes with core–shell structure were synthesized in this paper by semi-continuous seed emulsion polymerization. One latex was the random copolymer prepared by butyl acrylate (BA), methyl methylacrylate (MMA) and dodecafluoroheptyl methacrylate (DFHMA). The other latex was silica-containing fluoroacrylate copolymer prepared by the modification of above BA/MMA/DFHMA core–shell copolymer with the hydrolysis of tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$) in the presence of dodecyltrimethoxysilane (DTMS, $C_{12}H_{25}Si(OCH_3)_3$). The latexes were characterized by FT-IR, SEM-EDX, DSC, TEM and AFM.

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Crystalline aluminium hydroxy fluorides—Suitable reference compounds for ^{19}F chemical shift trend analysis of related amorphous solids

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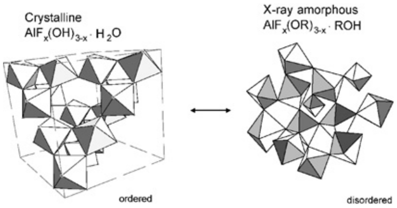

Well defined crystalline aluminium hydroxy fluorides $AlF_x(OH)_{3-x}$ were prepared with varying Al/F ratios through the sol–gel route followed by hydrolysis. Correlations between experimental ^{19}F MAS NMR-data and the average composition of AlF_xO_{6-x} species allowed a ^{19}F chemical shift trend analysis to be developed. The prediction of the average chemical surrounding of aluminium in related amorphous compounds is now possible, as there exist several similarities between crystalline $AlF_x(OH)_{3-x} \cdot H_2O$ and amorphous phases $AlF_x(OX)_{3-x} \cdot XOH$ (X = H, R (alkyl)).

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Fluorine-contained photoacid generators (PAGs) and corresponding polymer resists

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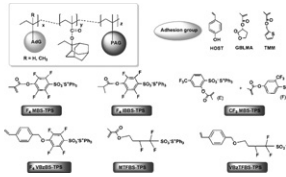

A new series of fluorinated anionic photoacid generators (PAGs) [methacrylate-substituted benzene sulfonic PAGs] (such as, F4-MBS-TPS, F4VBzBS-TPS, F4-IBBS-TPS, CF3 MBS-TPS, MTFBS-TPS and VBzTFBS-TPS), as well as corresponding PAG-bound polymeric resists (HS-EA-PAG) based on hydroxystyrene (HOST) and 2-ethyl-2-adamantyl methacrylate (EA), (GB-EA-PAG) based on γ-butyrolactone methacrylate (GBLMA) and 2-ethyl-2-adamantyl methacrylate (EA) were prepared in moderate to good yield and characterized. The acid generating efficiency of PAG bound polymers was in the range of 54–81%, which agrees well with the electron withdrawing effect of the substituents. With regard to the referenced F4-PAG bound polymer with 68% acid generating efficiency, and our previously reported EUVL results of F4-MBS-TPS bound polymer photoresists, these new PAG bound polymers should be effective resists for 193 nm or EUV lithography.

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Novel methacrylate copolymers with fluorine containing: Synthesis, characterization, reactivity ratios, thermal properties and biological activity

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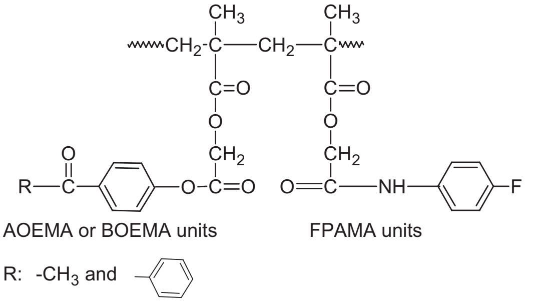

Novel methacraylate monomer with the side chain fluorine was synthesized and copolymerized with other new methacrylate monomers having pendant ketone.

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Synthesis and spectral properties of Eu^{3+}-doped YF_3 nanobundles

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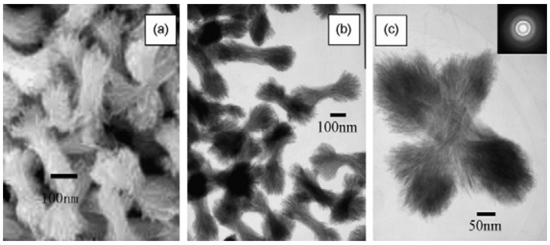

(a) SEM image of YF_3:Eu^{3+}(5%) nanobundles. (b) TEM image of nanobundles. (c) A crossed nanobundle; Inset: electron diffraction patterns.

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CF_3-substituted 1,3-dicarbonyl compounds in the Biginelli reaction promoted by chlorotrimethylsilane

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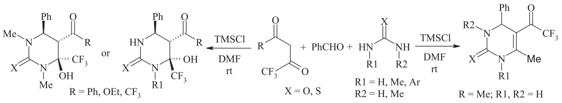

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Hexafluorosilicates of bis(carboxypyridinium) and bis (2-carboxyquinolinium)

Vladimir O. Gelmboldt[a], Larisa V. Koroeva[a], Eduard V. Ganin[b], Marina S. Fonari[c], Mark M. Botoshansky[d], Alim A. Ennan[a]

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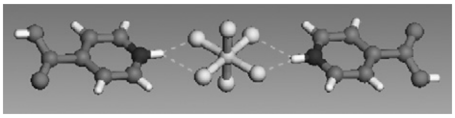

The preparation and characterization of three isomeric carboxypyridinium and carboxyquinolinium hexafluorosilicate salts is described. The compounds were studied by IR, mass-spectrometry, thermogravimetric analysis (TGA), and in one case by X-ray crystallography. The relationship between the salts solubility and the H-bonding system was analysed.

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Diastereoselective synthesis of cyclic 1,3-aminoalcohols bearing $CF_3(CCl_3)$-groups

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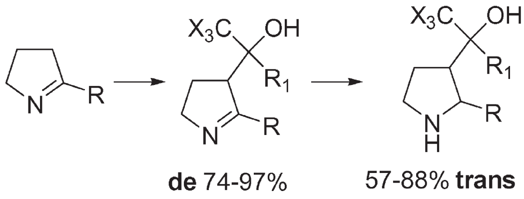

R=Alk, Ar, Het, OMe; R_1=CO_2Me, H; X=F,Cl

Reaction of cyclic imines and lactims with trifluoromethyl or trichloromethylcarbonyl compounds proceeded without any catalyst. The reduction of the prepared products leads stereoselectively to the 1,3-aminoalcohols containing pyrrolidine moiety.

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Effect of metal ion loaded in a resin towards fluoride retention

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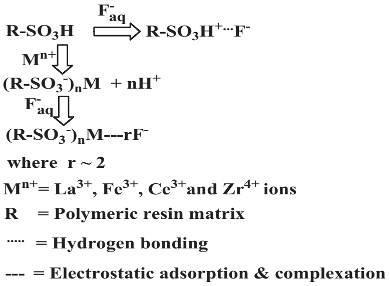
The metal (M = La^{3+}, Fe^{3+}, Ce^{3+} and Zr^{4+}) ion incorporated ion exchangers possesses higher defluoridation capacity than that of original resin with H^+ ion indicates its high selectivity towards fluoride. This is due to the presence of electrostatic adsorption and complexation between metal ion and fluoride whereas original resin which removes fluoride by hydrogen bonding.



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Improved thermal stability of crosslinked PTFE using fluorine gas treatment

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