Synthesis and Characterization of a Hyperbranched Hydrogen Bond Acidic Carbosilane Sorbent Polymer

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ABSTRACT: Sorbent polymers can be designed to target molecular interactions with a variety of hazardous chemicals including explosives, chemical agents, narcotics, and toxic industrial chemicals. Applications of functionalized sorbent polymers include preconcentrator devices, SPME fibers, membrane introduction systems, chromatographic stationary phases and coatings for chemical sensors. One common feature of a wide range of hazardous chemicals is their hydrogen bond (h-b) basicity. In this work, we report on the synthesis and characterization of a h-b acidic hyperbranched carbosilane fluoroalcohol based sorbent polymer (poly(methyldi(1,1,1-trifluoro-2-trifluoromethyl-2-hydroxypent-4-enyl)silane; HCSFA2), which is suitable for sorbing these hazardous h-b basic analytes. Multiple batches of HCSFA2 were characterized with routine composition, spectroscopic, thermal analysis, and inverse gas chromatography (iGC) to evaluate polymer physicochemical properties. In comparison with previously developed h-b acidic polymers (e.g., FPOL and SXFA), HCSFA2 exhibits a sorption improvement of 10–15 fold for h-b basic analytes. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 3000–3009, 2010

KEYWORDS: carbosilane polymer; chemical agent; explosive; HCSFA2; hydrogen bond acid, sorbent polymer; hyperbranched; inverse gas chromatography; sorbent

INTRODUCTION Trace level detection of toxic or hazardous chemicals including explosives, chemical agents, and toxic industrial chemicals (TICs) is an area of significant importance for military and civilian applications.[1–4] Applications for sorbent polymers in this area may include preconcentrator devices, SPME fibers, membrane introduction systems, chromatography, and gas or vapor sensors.[5–20] The focus of this work centers on the synthesis and characterization of sorbent polymers for h-b basic analytes. Of particular interest are hazardous chemicals including explosives and chemical warfare agents [e.g., 2,4,6-trinitrotoluene (TNT), cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX), triacetonetriperoxide (TATP), Sarin (GB), and Tabun (GA)].[10,21–29] In general, the low vapor pressure of these hazardous chemicals can make direct vapor detection challenging. Targeting the h-b basic solubility properties of these analytes, materials have been developed with complementary h-b acidic properties.[4,7,11–19,30–35] Sorbent polymer coatings with enhanced h-b acidic properties have been developed by the US Naval Research Laboratory (NRL) and others since the 1970s.[6,7,9,10,21–26,33–39] The early h-b acidic sorbent polymers incorporated hydroxyl derivatives including alcohol, carboxylic acid, or phenolic groups.[20,31,32] These polymers exhibited modest h-b acidic properties and also included significant inter- and intramolecular hydrogen bonding. More recently, addition of electron withdrawing halogens in close proximity to hydroxyl groups has allowed a dramatic increase in the h-b acidity with a concomitant reduction in the h-b basicity.[7,10–12,17–26,30–37,39–50]

In the design of these h-b acid polymers several physicochemical properties were considered. These include a glass transition temperature (T_g) at or below the anticipated application temperature, strong but reversible sorption of analyte, thermal and chemical stability at operating conditions, and the ability to target analytes of interest.[18,22,32,43,44,51] There have been three main phases of the work at NRL in sorptive polymers to take advantage of these properties. This includes the development of the h-b acidic fluoropolyol oligomer (FPOL),[39,52] h-b acidic polysiloxanes,[5,30,21–23,53] and more recently h-b acidic polycarbosilanes.[10,21–26,54–56] The switch from the ether linked FPOL oligomers to the hexafluoroisopropanol (HFIP) substituted siloxanes was aimed at improving the h-b acidity and decreasing the h-b basicity properties of the hydroxyl group.[17,33,43,45,54–56] The siloxane polymers developed include SXFA and SXFA2 which both offered low T_g properties suitable for rapid vapor sorption and functional groups with stronger h-b acidity when compared to FPOL.[23,32,40,45]

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14. ABSTRACT

Sorbent polymers can be designed to target molecular interactions with a variety of hazardous chemicals including explosives, chemical agents, narcotics, and toxic industrial chemicals. Applications of functionalized sorbent polymers include preconcentrator devices, SPME fibers membrane introduction systems, chromatographic stationary phases and coatings for chemical sensors. One common feature of a wide range of hazardous chemicals is their hydrogen bond (h-b) basicity. In this work, we report on the synthesis and characterization of a h-b acidic hyperbranched carbosilane fluoroalcohol based sorbent polymer (poly(methyldi(1,1,1-trifluoro-2-trifluoromethyl-2-hydroxypent- 4-enyl)silane; HCSFA2), which is suitable for sorbing these hazardous h-b basic analytes. Multiple batches of HCSFA2 were characterized with routine composition, spectroscopic thermal analysis, and inverse gas chromatography (iGC) to evaluate polymer physicochemical properties. In comparison with previously developed h-b acidic polymers (e.g., FPOL and SXFA), HCSFA2 exhibits a sorption improvement of 10-15 fold for h-b basic analytes.

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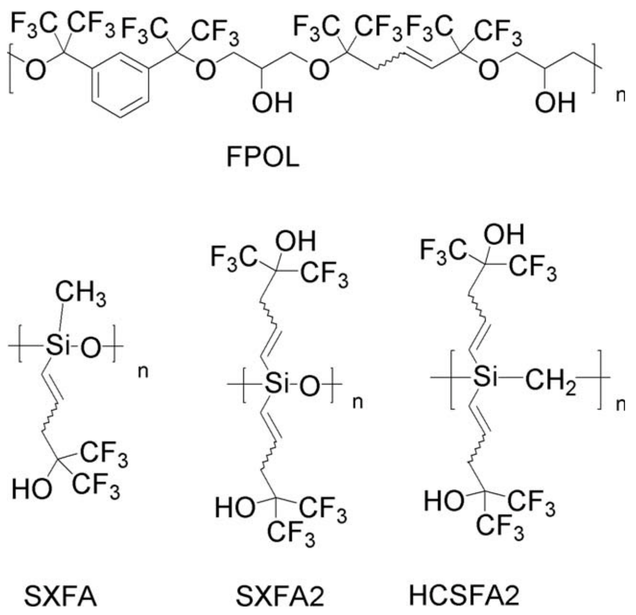

FIGURE 1 Comparison of FPOL, SXFA, SXFA2, and HCSFA2 structures.[17,19,21]

The recent development of hybrid carbosilane-siloxane and phenol based polymers such as BSP3, BSP6, and DKAP offer some improved sorbent characteristics compared to FPOL and SXFA.[43–45,47,53] However, the instability of the siloxane linkage remains a weakness that can lead to degradation of polymer properties over time. In addition, the siloxane backbone acts as an undesirable site for competitive binding with the HFIP groups or h-b acid analyte molecules.[4,16–19,30–32,44,48–50,52]

The synthesis of carbosilane polymers via a Grignard reaction was originally developed by Interrante and the hexafluoroacetone functionalization was developed by Urry.[51,54,55–57] Both procedures were incorporated here to obtain HCSFA2. Typically with this synthesis, molecular weights are relatively low with a degree of polymerization below 15.[57] In addition to employing a carbosilane polymer backbone in the synthesis reported here, the architecture of the polymer was modified. A trifunctional chlorosilane monomer was used to allow the synthesis of a polymer with a hyperbranched structure.[54–56] Hyperbranched polymers offer the advantage of increasing the exposure of their peripheral functional groups, decreased viscosity at ambient temperature, and ease of synthesis when compared with dendritic polymers.[28,45,51,54–56,58]

In this article we describe the detailed synthesis of a new h-b acid polymer based on the hyperbranched polycarbosilanes.[10,22,24–26] The polymer made and reported here has the acronym HCSFA2 where the acronym stands for hyperbranched carbosilane fluoroalcohol with two functional groups per silicon atom. Multiple batches of HCSFA2 were synthesized and are reported here to show the consistency of these polymers from batch to batch. HCSFA2 exhibits excellent physicochemical properties in a variety of analytical applications. We compare the sorption properties, using inverse gas chromatography, of HCSFA2 to other h-b acid sorbent polymers including FPOL and SXFA, and PDMS which is widely used as a sorbent material in analytical applications.

RESULTS AND DISCUSSION

Synthesis of HCSA2 and HCSFA2

The detailed synthesis of HCSFA2 has not been reported previously. The polymer synthesis was adapted from procedures developed by Interrante and Urry.[54–56] The HCSFA2 polymer is different from previously reported h-b acidic sorbent polymers in that this polymer is a hyperbranched carbosilane polymer (Figs. 1, 4). The HCSFA2 polymer was developed to improve h-b acidic properties, longevity, and thermal stability in air when compared with siloxane and ether linked polymers.[17,26–24] The purpose of the h-b acidic sites is to offer complimentary molecular binding sites for h-b basic target molecules including nitroaromatics, phosphonate esters, or toxic industrial chemicals (Fig. 2). The electron rich oxygen in these target molecules interacts with the very h-b acidic proton in the HFIP group to form a relatively strong hydrogen bond (Fig. 2).

The HCSFA2 synthesis procedure presented here has been modified and optimized to improve the physical properties and the reproducibility of the product (Fig. 3). The synthesis is a challenge due to the strict temperature requirements and the desire to improve polymer conversion. The polymer described here has been synthesized with variations in color, viscosity, and sorption performance depending on the specific synthesis conditions. However, with the procedure presented here we have obtained consistent and desirable results.

Synthesis of the HCSA2 [hyperbranched carbosilane allyl 2 allyls per monomer (**1**)] parent batches used the Grignard reaction at low (0 °C to ambient) temperature (Fig. 3).[51,54–56] The resulting intermediate allyl-pendant polymer (**1**) appeared cloudy due to the presence of residual salt. After evaporation of the solvent the polymer was redissolved in diethyl ether and the insoluble salts were then centrifuged out and the transparent solution filtered through Celite. The resulting parent polymer was then functionalized with hexafluoroacetone

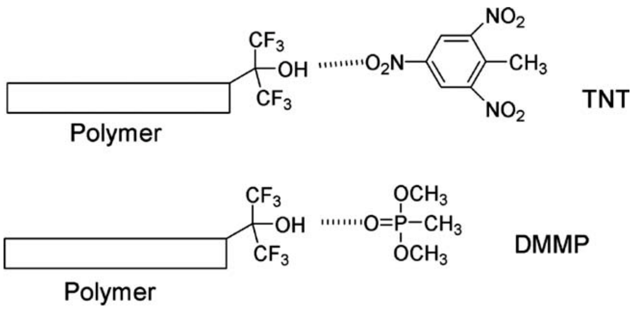

FIGURE 2 Hydrogen bonding (dashed line) of the h-b acidic polymer with h-b basic analytes.

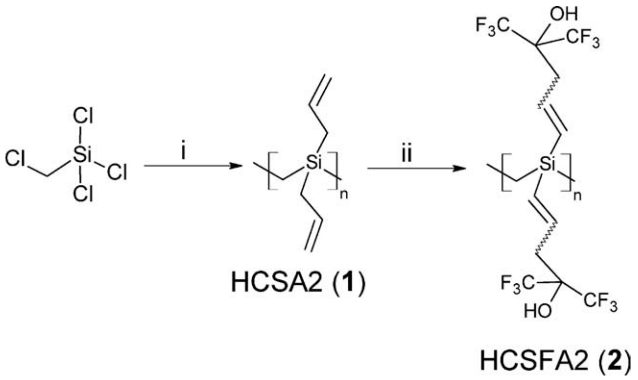

FIGURE 3 Synthesis of HCSFA2. (i) 1: Mg, SiCl4, THF, 0–25 °C, 24 h; 2: THF, allyl magnesium bromide 25 °C, 24 h. (ii) 1: CHCl3, hexafluoroacetone; 2: 60 °C, 24 h.

(HFA) at 60 °C for 24 h. The HFA functionalization mechanism is a modified "ene" synthesis.[59] The double bond of HCSA2 (**1**) electrophilically attacks the ketone carbon of the HFA. The bonds are formed via a pericyclic mechanism which requires formation of a six membered ring[59] which may explain why in X-ray crystallographic analysis of model compounds there appears to be a majority of cis double bonds.[58] Complete functionalization may be hampered due to the steric hindrance of the six membered ring in the interior of the hyperbranched polymer.

For simplicity HCSFA2 is drawn in linear form in Figures 1 and 3, but because of the trifunctional monomer, the polymerization produces a hyperbranched architecture represented by the chemical structure in Figure 4. For the synthesis of HCSA2 it is very important to keep control of the reaction temperature at or below room temperature. After the reaction with HFA, the polymer can be repeatedly heated to elevated temperatures.[10,22]

Spectroscopic Characterization of HCSFA2

HCSFA2 was made in different batches with the representative samples from 2004 (A) and 2007 (B) used here. All FTIR and NMR spectra reported here were for HCSFA2 B and the corresponding HCSA2 parent unless otherwise noted. FTIR spectra for HCSFA2 compared with HCSA2 (Fig. 5) shows the parent includes C-H (sp^2 3050 cm^{-1}), C=C at 1640 and 800 cm^{-1}, CH aliphatic at 2950 cm^{-1}, and SiC at 1200 cm^{-1}. After reaction with HFA, the HCSFA2 spectrum changes with the appearance of OH (3700, 3500br, 3200sh cm^{-1}), CF (1250 cm^{-1}) and shifts of the C=C peaks associated with the allyl groups (3050, 1600, 700–800 cm^{-1}). Another interesting observation is the asymmetric OH (3700, 3400, 3200 cm^{-1}) in the FTIR of HCSFA2 (Fig. 5 bottom). This can be attributed to free, associated, and hydrogen bonded OH groups from the HFIP.

NMR Results of HCSFA2

The ^{1}H NMR of the parent HCSA2 [Fig. 6(a)] showed peaks for the CH_2 in the backbone 0.5 ppm, allylic CH_2 1.5–2.0 ppm, olefinic CH_2 at 5.0 ppm and CH in the double bond 5.8 ppm. The CH_2 in the backbone (0.5 ppm) provides a broad peak because of several different environments including backbone CH_2 and terminal CH_3. There may be traces of unreacted CH_2—Cl (2.8 ppm). The CH_2 of the allyl group (1.5–2.0 ppm) was split due to cis and trans isomers of the double bond.

The ^{1}H NMR of HCSFA2 [Fig. 6(a)] had residual acetone, diethyl ether, and THF, which were the small peaks at 2.0, 3.6, and 4.3 ppm. The peak for the terminal CH_2= from the allyl in HCSA2 shifted from 1.5–2.0 ppm to 2.5–3.0 ppm for —CH_2— in HCSFA2. The —CH_2— protons shift due to the increased electron withdrawing groups from the adjacent HFIP. There are also peaks associated with the —CH=CH— in HCSFA2 at 6.0 and 6.5 ppm. The peaks for the —CH=CH— overlap slightly with traces of unreacted allyl groups (5.0 and 5.6 ppm).

^{13}C NMR of the parent polymer [Fig. 6(b) top] had peaks for the CH_2 backbone (0 ppm), CH_2 allylic (25 ppm), vinylic CH (115 ppm), and CH_2 (135 ppm). The HFA functionalized polymer [Fig. 6(b) bottom] had peaks associated with —CH_2— (34 ppm), CH=CH (135 and 140 ppm), and the appearance of peaks associated with $C(CF_3)_2OH$ (76 ppm), and CF_3 (120–130 ppm). The backbone CH_2 was at ~0 ppm

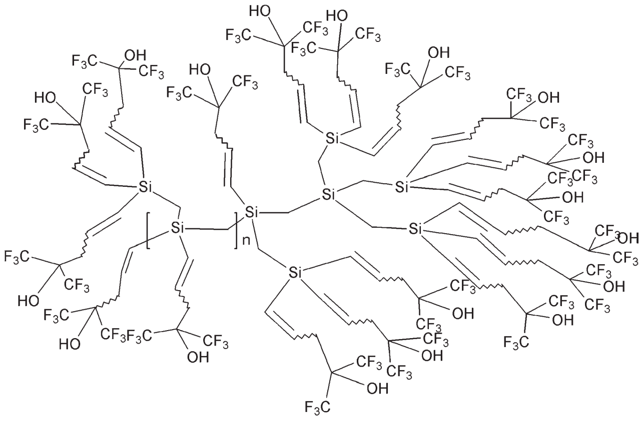

FIGURE 4 Cartoon of hyperbranched architecture of HCSFA2.

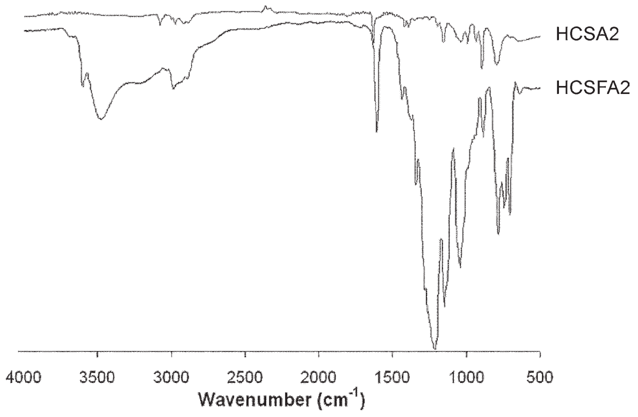

FIGURE 5 FTIR of HCSA2 (1) (bottom) and HCSFA2 (2) (top).

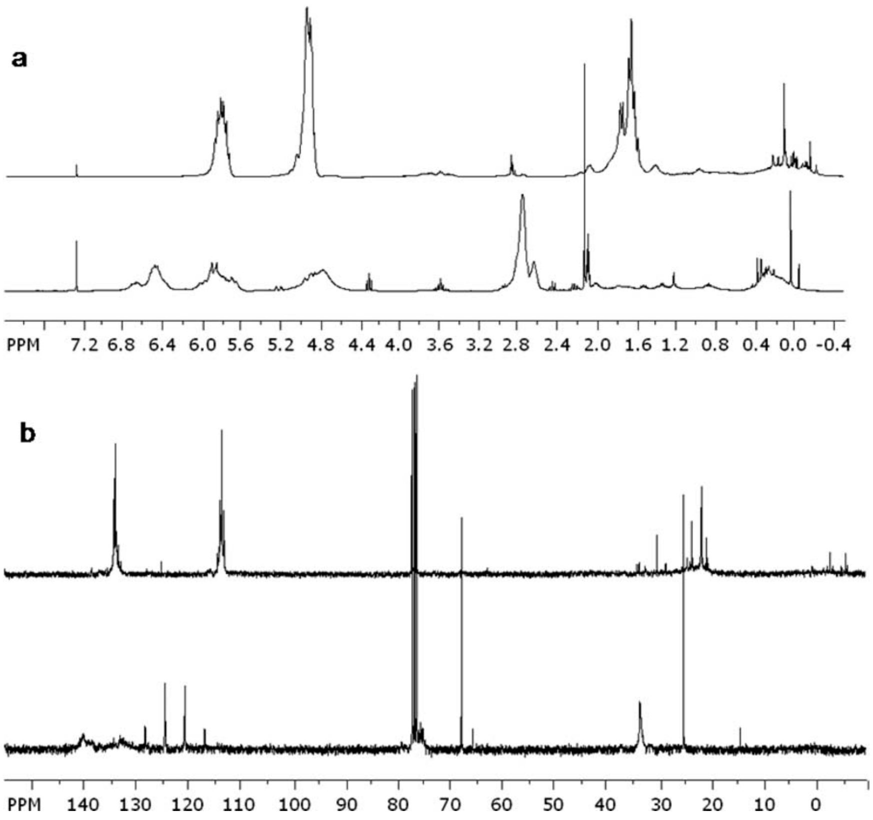

FIGURE 6 (a) ^{1}H NMR of HCSFA2 (bottom) and HCSA2 (top) and (b) ^{13}C NMR of HCSFA2 (bottom) and HCSA2 (top).

but broadened significantly. There are two sets of peaks at 14.5, 25, 65, and 67 ppm which are residual THF and ether. ^{19}F NMR shows a single peak at -76.8 ppm. Finally, ^{29}SiNMR of HCSFA2 had peaks at -8.5, -21, -33.3, and -51.5 ppm. (Fig. 7 bottom) and HCSA2 had only one major peak at -0.3 ppm (Fig. 7 top). Based on these peaks the predominant single silicon environment in HCSA2 becomes multiple environments including cis/trans and vinylic shifts of the carbons around silicon. In addition, peaks for HCSFA2 are located further upfield from zero compared with HCSA2. Figure 8 shows the ^{1}H NMR of HCSFA2 after heat treatment at 170 °C for 30 min. There was no change or shift in peak position and integration for the polymer after heat treatment.

Physical Characterization of HCSFA2 and HCSA2

Gel permeation chromatography (GPC) provides a relative molecular weight comparison to linear polystyrene standards. In this case HCSFA2 had an M_w of 1804, M_n of 791 and PDI of 2.3 which was determined in THF. Molecular weights are low and can be partially attributed to the hyperbranched nature of the polymer. The molecular weights determined here are comparable to those reported by Interrante[57] for HCSA2. Elemental analysis for HCSFA2 showed elevated values for H, 3.1% and C, 35.4% compared with the theoretical weight percents of H, 2.2%, and C, 34.3%. Fluorine composition numbers were depressed with a value of 47.1% when compared with a theoretical of 50.2%. This may be attributed to incomplete HCSA2 polymer reaction with HFA (>95% by ^{1}H NMR).

Viscosity values for the parent and functionalized polymers were determined to evaluate their suitability for high

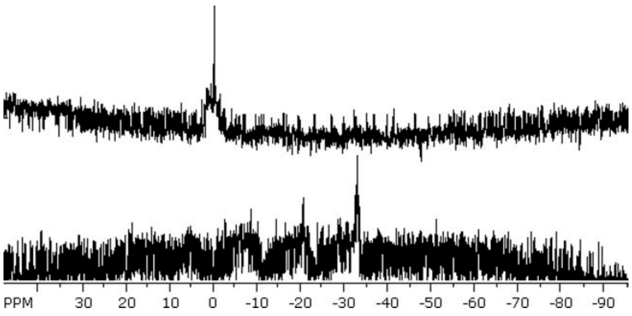

FIGURE 7 ^{29}Si NMR of HCSA2 (top) and HCSFA2 (bottom).

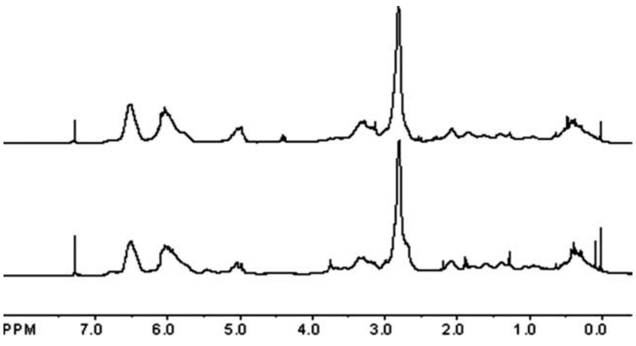

FIGURE 8 ^{1}H NMR comparison of 30 min heat treated HCSFA2 (bottom) and unheated HCSFA2 (top).

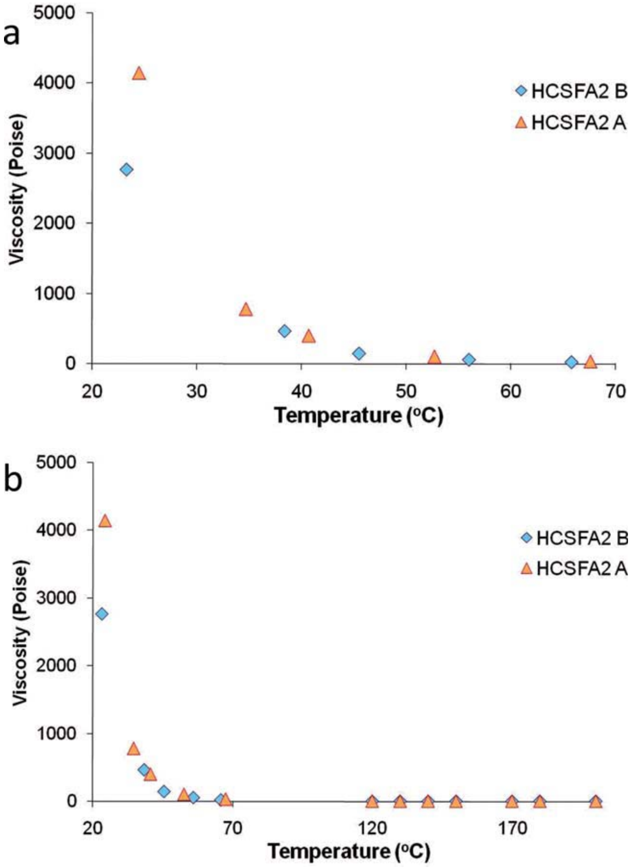

FIGURE 9 HCSFA2 viscosity comparison. (a) experimental data and (b) showing extrapolated data points above 120 °C.

temperature applications and for consistency between polymer batches. Viscosity values for HCSA2 and HCSFA2 were found to be 20 cP and $\sim 3.2 \times 10^5$ cP respectively at 25 °C. HCSFA2 polymers also showed Newtonian fluid behavior with a linear increase in shear stress observed as a function of shear rate. The viscosities of both batches of HCSFA2 decreased with increasing temperature to similar values above 55 °C [Fig. 9(a)]. The viscosities of the HCSFA2 polymers were extrapolated from 120 to 200 °C, the highest operation temperature for many analytical applications, with a calculated value of 500 cP [Fig. 9(b)].

Thermal Study of HCSFA2 Polymers

Differential scanning calorimetry (DSC) was utilized to determine the T_g of HCSFA2. This was observed as a weak transition at −8 °C. For comparison, FPOL and BSP3 (phenolic siloxane) have reported T_g values of 16 and 6 °C respectively.[31,47,60] The lower T_g for HCSFA2 provides a wider temperature range for effective vapor sorption.

The thermal stability of HCSFA2 was determined by TGA as the 5% weight loss temperature (WLT). During initial experiments with HCSFA2 in heated applications we observed outgassing of one or more low molecular weight species. These volatiles decreased if a thin coating of HCSFA2 (1–5 microns) was cycled between ambient and 170 °C for a short time. In order to further purify HCSFA2 before determining the thermal stability a series of heat/hold TGA experiments were conducted to precondition and eliminate the volatile component(s). HCSFA2 A, HCSFA2 B, SXFA, and FPOL were separately heated to 170 °C for 30 min and then heated to decomposition (Table 1). During this initial heat/hold purification step HCSFA2 lost 5–10 wt % whereas FPOL and SXFA lost ~15 wt %. The thermal stability of HCSFA2 was subsequently determined as ~270 °C. The high thermal stability of HCSFA2 provides useful properties for high temperature applications including those that require repeated thermal cycling in air.

Rates of weight loss are shown in the TGA derivative thermogravimetry (DTG) curves in Figure 10. The peak maxima in the DTG corresponds to the largest rate of weight loss. Without the heat/hold step, the two batches of HCSFA2

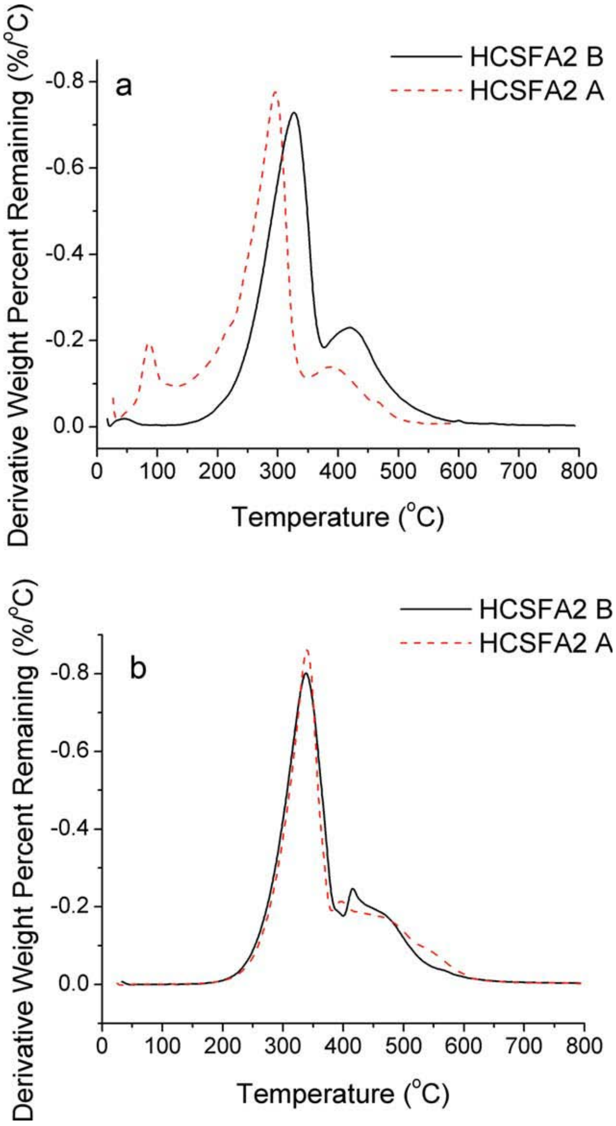

FIGURE 10 DTG TGA curves for different HCSFA2 polymers (a), and DTG TGA curves for heat/hold treated HCSFA2 polymers (b).

TABLE 1 Thermal Stability of HCSFA2 Polymers and Heat/Hold Results

Polymer	5% WLT (°C)	Weight Loss During Heat Hold (wt %)	5% WLT After Heat/Hold (°C)
HCSFA2 A	159	10	277
HCSFA2 B	185	6	260
SXFA	196	16	240
FPOL	164	14	263

exhibited multiple features offset by about 50 °C [Fig. 10(a)]. After the heat/hold treatment, the first DTG peak maxima were essentially identical at 350 °C. The sorptive properties of these polymers were not adversely affected by the heat treatment. Supporting evidence is provided from the iGC data presented in the next section.

Inverse Gas Chromatography Experiments

A series of experiments were performed with an inverse gas chromatograph to obtain additional physicochemical properties of the polymers. Inverse gas chromatography (iGC) has been used to characterize and screen potential polymers for a variety of analytical applications including sorbent coated sensors, chromatographic columns, and preconcentrator devices.[41,42,50,61] iGC is performed by injecting individual solutes with known physical and chemical properties into a gas chromatographic column which uses a polymer with unknown properties as the stationary phase. The degree of molecular interaction between the polymer (solvent phase) and solute directly affects the elutant times and influences peak profiles. The resulting chromatograms can be used to compute a number of thermodynamic parameters. iGC has been used to determine a wide range of parameters for polymers including: dispersive surface energy (γ), specific free energy (ΔG_{sp}), polymer-gas solute partition coefficients (K), heat of sorption (ΔH_{sp}), acid and base dissociation constants (K_a and K_b), degree of crystallinity, T_g, T_m, degree of crosslinking, activity coefficients, and interaction parameters for polymer–polymer systems.[41,42,59,62–66] In this article we compute the dispersive and specific surface energies, heat of sorption, and used the iGC retention properties to calculate the polymer-gas partition coefficients for h-b basic solutes. HCSFA2 iGC results are compared with FPOL, SXFA, and PDMS. Parameters generated by iGC assume that the experiments are carried out at infinite dilution, so that the only observed interactions are representative of the solute and polymer. Additional details of iGC theory are reported elsewhere.[42,60–66]

The retention volume of a solute V_n can be related to the dispersive component of the surface energy of the solute probe γ_L^D and the polymeric stationary phase, γ_P^D. The polymer γ_P^D values can be obtained from the slope of the line found by plotting $RT{\cdot}\ln(V_n)$, for a series of *n-alkane* probes, versus $a{\cdot}[\gamma_L^D]^{0.5}$ [42,60,62,63]. Here, R is the ideal gas constant, T is the absolute temperature of the column, and a is the surface area of the solute probe. The $a{\cdot}[\gamma_L^D]^{0.5}$ values for *n*-alkanes are available in the literature.

For a polar solute, and using the same plot, the vertical distance between the polar probe data point and the reference n-alkane line represents the specific polar component of the free energy of sorption, ΔG_{sp}. In addition, by plotting ΔG_{sp} for individual solute probes, the specific enthalpy, ΔH_{sp}, and the specific entropy, ΔS_{sp} of sorption can be computed[42,60,62,63]. The dispersive surface energies of HCSFA2 batches A and B were 32 and 34 mJ/m^2 respectively (Table 2). This indicates that batch B provides a modest increase in nonpolar interactions when compared with A. This may result from a less complete functionalization for B compared to A. Comparable values of dispersive surface energy for HCSFA2 were observed at 80% RH (32 mJ/m^2) and 0% RH value (34 mJ/m^2). FPOL and SXFA both provide higher dispersive surface energies (37 mJ/m^2) when compared with HCSFA2.

By injecting polar solutes with known solubility properties into the iGC column, the $-\Delta G_{sp}$ values for solute-polymer combinations were determined. Larger values of $-\Delta G_{sp}$ are characterized by longer retention times and indicate presence of stronger intermolecular forces.[54,59] In this work, acetone, methanol, 2-propanol, chloroform, and acetonitrile were selected as solute probes. For simplicity only the results from acetone are presented here. Acetone is a mid range h-b basic analyte with a h-b basicity (β_2) of 0.49.[67] In comparison, phosphonate esters all have larger h-b basicity values ($\beta > 0.78$).[68,69] HCSFA2 batches A and B provided $-\Delta G_{sp}$ (acetone) values of 21.5 and 22.0 kJ/mol, respectively. In comparison FPOL, SXFA, and PDMS provided significantly lower $-\Delta G_{sp}$ values of 13.0, 15.5, and 8.0 kJ/mol, respectively, (Table 2). When considering the logarithmic relationship of these values and analyte polymer-gas partition coefficients[35] these results illustrate the significantly higher sorption properties for HCSFA2 with h-b basic analytes. The HCSFA2 polymers were also examined by iGC at high humidity levels to determine if there is a significant influence of

TABLE 2 iGC Surface Energies for HCSFA2 Other Sorbent Polymers

Polymer	Dispersive Surface energy (γ_P^D) (mJ/m^2)^a	$-\Delta G_{sp}$ Acetone (kJ/mol)^a
PDMS	27	8.0
FPOL	37	13.0
HCSFA2 A	32	21.5
HCSFA2 B	33	22.0
HCSFA2 B (80% RH)	32	23.1
HCSFA2 B after heat/hold 170 °C 30 min	38	21.0

[a] Error = ±1 mJ/m^2 for dispersive and ±0.5 kJ/mol for $-\Delta G_{sp}$ based on five measurements of the same sample.

the water on sorption of h-b basic analytes. A modest influence of humidity (80% RH) was found for the HCSFA2 sorption of acetone (23.1 kJ/mol).

Finally, the HCSFA2 polymer that was heat treated at 170 °C for 30 min was also examined by iGC to determine if there were any changes in the sorptive properties after heat/hold treatment. The iGC results show that the sorption properties for HCSFA2 remained essentially unchanged (22.0 originally vs. 21.0 kJ/mol after thermal treatment).

Enthalpy (ΔH_{sp}) measurements were determined by iGC for single probe molecules tested over a range of temperatures. Typical ΔH_{sp} values are exothermic for sorption of polar molecules into polymers,[64,66] and for HCSFA2 ΔH_{sp} (acetone) was found to be -34.52 kJ/mol. ΔS_{sp} (change in entropy) can be simply computed from $\Delta G_{sp} = \Delta H_{sp} - T\Delta S_{sp}$ to give $\Delta S_{sp} = -0.041$ kJ/mol K at 298 K. The negative ΔS_{sp} implies slight ordering when the polymer interacts with acetone.

Polymer-gas partition coefficients (K) were calculated for acetone using the equation: $\Delta G_{sp} = -RT\ln(K)$ where R is the gas constant (8.314 J/mol·K), and T is the temperature in Kelvin. K values quantify the sorptive interaction between the solute vapor (acetone) and polymer (HCSFA2) and are simply computed from $K = C_p/C_v$. Where C_p is the concentration of the analyte in the polymer and C_v is the concentration of the solute in the gas phase. A larger K indicates stronger intermolecular forces present between solute and polymer.[21]

K values at 30 °C were determined for acetone for each polymer using iGC retention properties and are plotted in the bar graph in Figure 11. PDMS provides a K value of 25 and SXFA and FPOL offer K values in the hundreds with SXFA ($K = 451$) being more than double that of FPOL ($K = 181$). HCSFA2 batches A and B ($K = 4890$ and 6718, respectively) demonstrated K values 15 times stronger than SXFA. After a heat treatment the K value for HCSFA2 ($K = 4341$) was still approximately an order of magnitude larger than that of SXFA. The significantly stronger sorption properties of HCSFA2 for acetone reflect the improved availability and h-b acidic properties of HCSFA2 when compared to the other tested h-b acidic polymers (SXFA and FPOL). HCSFA2 K values for acetone are ~200 times stronger than the relatively nonpolar PDMS polymer. The marked improvement in K values for HCSFA2 and acetone over other h-b acidic sorbents and PDMS tested here support its potential as a sorbent material for h-b basic analytes, such as the nitro aromatic explosives or phosphonate ester nerve agents. A relatively low T_g value offers a wide temperature range for effective vapor sorption. The high thermal stability of HCSFA2 allows its use in applications requiring high temperatures or thermal cycling. In one study, HCSFA2 has been repeatedly heated to 180 °C in laboratory air for 2,841,113 cycles without an apparent degradation in sorption properties.[10] Due consideration should be made for the low viscosity properties provided by HCSFA2 at elevated temperatures. For applications requiring structural integrity of the sorbent material, such as a membrane, cross linking strategies or structural filler options may offer a viable path to utilize HCSFA2.

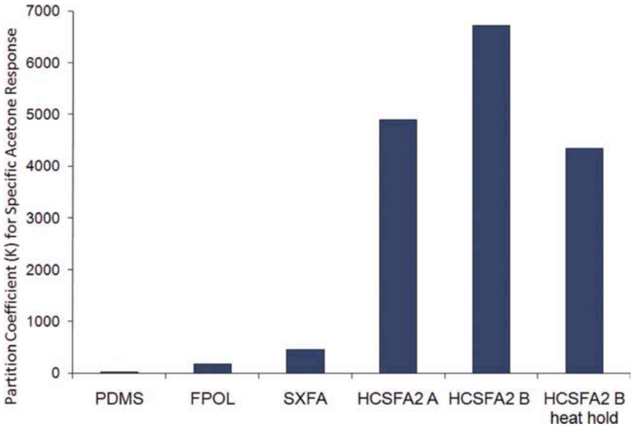

FIGURE 11 Determination of acetone vapor/polymer partition coefficients (K) for various polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

EXPERIMENTAL

Materials and Methods

All chemicals were used as received unless otherwise noted. Mg^o, $SiCl_4$, $CHCl_3$ (99+%), diethyl ether (99+%), THF (99.8%), acetone (99%), NH_4Cl, allyl magnesium bromide 1 *M* in diethyl ether, Celite®, and hexafluoroacetone (HFA, 98%) and all other chemicals were from Sigma-Aldrich Chemical unless otherwise noted. Chloromethyl trichlorosilane ($ClCH_2SiCl_3$) (Gelest) and other air sensitive reagents were handled under N_2 atmosphere and Schlenk techniques at all times to prevent hydrolysis. THF (Sigma-Aldrich Chemical, HPLC grade) was distilled from sodium-benzophenone ketyl under nitrogen. Silanized glass wool and presilanized 30 cm by 3 mm i.d. glass columns were from Surface Measurement Systems (SMS) iGC probe vapors—n-undecane, n-decane, n-nonane, n-octane, n-heptane, acetone, methanol, 2-propanol, acetonitrile, and $CHCl_3$ were all anhydrous from Sigma-Aldrich Chemical. The iGC carrier gases used were ultra high purity grade from Airgas.

^{1}H, ^{29}Si, 19F, and ^{13}C NMR spectra were collected with a 300 MHz Bruker ATS NMR. FTIR spectra were collected with a Digilab FTS 7000e using KBr salt plates and a liquid N_2 cooled MCT detector. TGA experiments were conducted with a TA Instruments TA 2950 with typical experiments heating the polymer (~10 mg) at 20 °C/min from room temperature to 800 °C. DSC experiments were conducted with a TA Instruments TA 2920 DSC heating the polymer from RT to 150 °C cooling to −100 °C, and heating at a rate of 10 °C/min to 160 °C to record data for T_g and T_m. The iGC experiments were performed with an SMS 6890*N* inverse gas chromatograph at 30 °C with specific experiments described below. Data was recorded with SMS iGC v1.8 and ChemStation software, and analyzed using Microsoft Excel and SMS iGC software. Viscosity measurements were taken with a Brookfield DVII+ Pro viscometer using an LV-4 spindle. Elemental Analysis (C, H, F) was carried out by Galbraith Laboratories. GPC analysis was carried out by NSL Analytical Laboratories.

Synthesis of HCSA2 (Parent, 1)[54,56,57]

Mg^o (~5 g, 200 mmol) was stirred in a 500 mL round bottomed flask and dried overnight under reduced pressure. 0.1 mL (0.149 g, 0.9 mmol) $SiCl_4$, and then 15 mL (22.0 g, 120 mmol) of $ClCH_2SiCl_3$ were added with rapid stirring at room temperature and the reaction temperature maintained at or slightly below room temperature using an ice/water bath for 8 h. (Caution! This reaction can generate significant heat and requires monitoring). Freshly distilled THF (1–5 mL) was added as required to adjust for viscosity and allow stirring. The reaction mixture was stirred overnight at room temperature without the water bath. After 12–24 h the reaction was cooled to 0 °C, THF was added, and 250 mL of 1 M allyl magnesium bromide (250 mmol) was added in 20 mL increments over 3 h. The reaction mixture was stirred at room temperature for another 24 h.

Finally, the reaction was quenched with 0 °C NH_4Cl (aq.). The aqueous layer was rinsed twice with THF followed by hexane and the organic layer was filtered through a packed bed of Celite® filter agent. The solvent was removed by rotary evaporation and the resulting HCSA2 polymer was re-extracted into ether, centrifuged and dried at room temperature under vacuum. The temperature of the parent polymer was maintained close to ambient temperature to avoid undesirable crosslinking. There were two parent batches A (made in 2004) and B (made in 2007), with B characterization being reported here. Yield: 13.96 g, (112 mmol, 93.2%) with >95% CH_2Cl groups reacted by ^1H NMR. FTIR (KBr, cm^{-1}): 3077, 2950, 1630, 1253, 794.

^1H NMR (300 MHz $CDCl_3$, δ): 0.07 (b, 2H, $Si{-}C\mathit{H}_2$ backbone), 1.68 (dd, 4H, 2 $Si{-}C\mathit{H}_2{-}$), 4.92 (m, 4H, 2 $C\mathit{H}_2{=}$), 5.80 (q, 2H, 2 $CH_2{-}C\mathit{H}{=}CH_2$) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, δ): −6 to 0.48 ($Si{-}\mathit{C}H_2$ backbone), 20–25 (${-}Si{-}\mathit{C}H_2{-}CH{=}$), 113 (${-}CH_2{-}\mathit{C}H{=}$), 134 ($\mathit{C}H_2{=}CH{-}$) ppm. $^{29}Si{-}NMR$ (300 MHz, $CDCl_3$, δ):−0.33 ppm. TGA 5% WLT = 121 °C.

Synthesis of HCSFA2 (Functionalized, 2)[55]

The parent polymer (HCSA2 (**1**)) (6 g, 40 mmol) was weighed into a stainless steel reactor and 20 mL of $CHCl_3$ was added. The reaction vessel was sealed with a valve and evacuated briefly. A gas cylinder of HFA was attached with Swagelok™ fittings to the reactor. The vessel was cooled with liquid N_2 and HFA was added (20 g, 120 mmol) to the parent polymer solution and the HFA cylinder was removed. After removal from liquid N_2 the reactor was allowed to warm to room temperature and then moved to a magnetically stirred oil bath heated at 60 °C for 24 h.

The reaction was cooled to room temperature and excess HFA was recovered under vacuum. The reactor was opened and rinsed three times with $CHCl_3$ to remove the polymer. The polymer solution was filtered through Celite®. The Celite® was washed three times with $CHCl_3$ and the volatiles were removed. The functionalized polymer was extracted into diethyl ether and subsequently dried under vacuum with heating. Theoretical yield = 22.6 g (assuming 2 HFA units per monomer), actual = 19.2 g (85%) with <5% of original allyl groups remaining by ^1H NMR. Elem. Anal. found: C, 35.4%; H, 3.1%; F, 47.1%; theoretical: C, 34.3%; H, 2.2%; F, 50.2%. FTIR (KBr, cm^{-1}): 3700, 3500, 3300, 2933, 1609, 1213, 1147, 1040, 700.

^1H NMR (300 MHz, $CDCl_3$, δ): 0.31 (m, 2H, $Si{-}C\mathit{H}_2$ backbone), 2.80 (b, 4H, 2 ${-}CH{-}C\mathit{H}_2{-}C$), 3.24 (b, 2H, $O\mathit{H}$), 5.05 (b, 0.5H, $CH_2{=}CH{-}$ (unreacted)), 5.97 (b, 2H, 2 $Si{-}C\mathit{H}{=}CH$), 6.50 (b, 2H, 2 $CH{=}C\mathit{H}{-}CH_2$) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, δ): 0 (CH_2 backbone), 33.7 ($\mathit{C}H_2{-}C(CF_3)_2OH$), 75–76 ($\mathit{C}(CF_3)_2{-}OH$), 117-128 (${-}\mathit{C}F_3$), 133 (${-}Si{-}\mathit{C}H{=}$), 140 (${-}CH_2{-}\mathit{C}H{=}$) ppm. $^{29}Si{-}NMR$ (300 MHz, $CD_3C(O)CD_3$, δ): −8.5, −21, −33.3, −51.5 ppm. ^{19}F NMR (300 MHz $CDCl_3$, d):δ): −76.82 ppm. GPC: $M_w = 1804$, $M_n = 791$, PDI = 2.3 in THF relative to polystyrene. TGA 5% WLT = 185 °C.

iGC Experiments with HCSFA2

HCSFA2 was coated on glass beads by dissolving 0.2 g HCSFA2 in ~50 mL $CHCl_3$ containing 3.8 g glass beads. The solution was stirred overnight, and solvent was removed under vacuum for 3–4 h. The HCSFA2 coated beads (0.1–0.5 g) were packed into a glass iGC column and retained by silanized glass wool. The actual weight percent of polymer on the glass beads was determined by TGA and was approximately half that of the calculated value. (The actual weight values determined by TGA were used for iGC calculations). The column was conditioned at 30 °C for 2 h before sequentially injecting probe vapors. The iGC was operated with He as the carrier gas (450 mL/min) and with a flame ionization (FID) detector. The temperatures of the injector and detector were 80 and 250 °C respectively. Experiments were conducted by injecting probe vapors, generated from liquid samples held at 30 °C, from a sample loop (0.25 mL) and diluted to 0.03 p/p^o (p/p^o = concentration of vapor/concentration of vapor at saturation). Experiments at higher humidity were performed at 80% relative humidity (RH) with acetone as the probe solute with all other test parameters remaining the same as the experiments conducted under dry conditions. Heats of sorption were computed with the iGC using the same column used at various column temperatures from 303 to 318 K with acetone as the probe solute.

Thermal Experiments with HCSFA2

HCSFA2 was heated in air to decomposition at a rate of 20 °C/min from room temperature to 800 °C to determine the thermal stability. In a separate experiment the polymer was heated to 170 °C for 30 min and the remaining polymer was reheated and decomposed in the TGA (RT-800 °C, 20 °C/min) or collected for characterization.

^1H NMR for 30 min at 170 °C heated HCSFA2 (300 MHz, $CDCl_3$, ppm): δ 0.15–0.63 (b, 2H, $Si{-}C\mathit{H}_2{-}$ backbone), 2.81 (b, 4H, 2 = $CH{-}C\mathit{H}_2{-}C$), 3.28 (b, 1H, OH), 5.03 (b, 0.6H $\mathit{C}H_2{=}CH{-}$ unreacted), 5.47 (b, 1H, $CH_2{=}C\mathit{H}{-}$ unreacted), 5.95 (b, 2H, 2 $Si{-}C\mathit{H}{=}CH$), 6.50 (b, 2H, 2 $Si{-}CH{=}C\mathit{H}{-}$).

CONCLUSIONS

We report the detailed and optimized synthesis for a functionalized h-b acidic polymer, HCSFA2. This polymer demonstrates a significant improvement in h-b acidity for sorbing h-b basic analytes when compared with other h-b acid polymers such as FPOL and SXFA. The synthesis of HCSFA2 is challenging, but under carefully monitored conditions reproducible physicochemical properties of the polymer were achieved. The parent polymer synthesis was found to be sensitive to temperature and side reactions were observed if the polymerization temperature was allowed to rise above room temperature. After removal of volatile components in the initial HCSFA2 product, the thermal stability for HCSFA2 was observed between 260–280 °C and allows its use in high temperature applications including those which require repeated thermal cycles in air. The improved sorptivity of HCSFA2 for acetone, as a representative hydrogen-bond base, was characterized with iGC and was found to be 250, 37 and 15 times higher than PDMS and the h-b acidic polymers FPOL and SXFA, respectively.

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