SYNTHESIS OF FLUOROHYDROCARBON DERIVATIVES OF HYPERBRANCHED POLYCARBOSILANES

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Introduction

Fluorocontaining polymers attract much attention due to the combination of the very specific properties. Low surface energy, chemical inertness, solubility in supercritical CO_2 allows to consider this combination as unique[1]. Among different variants of fluorocontaining polymers synthesis, the significant place belongs to a method highly functional polymeric matrixes modification by fluorocontaining agents[2]. In between number of various methods described in literature for such modification hydrosilylation has many benefits. Indeed the high reactivity of the reagents convenient kind of chemical process – addition reaction, and most important very good spectroscopic control after process conversion. In it's turn hyperbranched polyallycarbosilane (**HbPACS)** is an excellent matrix for further modification due to high functionality and reactivity of allylic groups in hydrosilylation process[3]. If we add to the consideration good solubility in most of the organic solvents and well established data of molecular organization in solution[4] it clear that both process and matrix are promising objects for the investigation. The goal of this work consisted in synthesis fluorocontaining hyperbranched polymers using different chemical agents for the modification. The effectiveness of the methods of modification and study of fluorocontaining polymers properties investigation were on the focus of this work. In this paper the synthesis of modifiers, comparison of the particular strategy of the modification and some properties of prepared polymers will be consistently considered.

Experimental

Materials. $HSi(CH_3)_2Cl$ was distilled directly prior to use. Organic solvents: toluene, hexane, ethanol, methanol were dehydrated by boiling and distilling over calcium hydroxide, THF were dried over CaH_2 and distilled from $LiAlH_4$. A xylene solution (2.1-2.4% Pt) of the (divinyltetramethyldisiloxane) platinum(0) complex (Aldrich) was used as the catalyst.

Instrumentation. ^1H NMR spectra were recorded on a Bruker WP-200 SY instrument (200.13 MHz) using tetramethylsilane as the internal standard.GPC analysis was performed on a Shimadzu instrument with a RID-10A refractometer and a SPD-M10AVP diode matrix as detectors using 7.8×300 mm Phenomenex columns (USA) filled with the Phenogel sorbent with pore sizes of 500 Å and THF as the eluent. Gas-liquid chromatographic (GLC) analysis was done on a 3700 chromatograph (Russia). A thermal conductivity cell was used for detecting signals; the carrier gas was helium; columns 2 m ¥ 3 mm were used ; the stationary phase was SE-30 (5%) supported on a "Chromaton-H-AW" sorbent. Chromatograms were processed using a "CI-100A" computer-controlled integrator (Czechia).

Hyperbranched polycarbosilanes. Hyperbranched polycarbosilanes was synthesized as described elsewhere[3].

Sodiumoxy-tris(γ-trifluoropropyl)silane(1). A solution of NaOH (4.88 g, 0.12 mol) in methanol (34mL) was added to the stirred solution of tris(γ-trifluoropropyl)disiloxane (40.0g, 0.061mol) in acetone (100mL) and toluene (300mL). The reaction mixture was boiled with removing acetone, methanol and water. After overall removing of water the reaction mixture was boiled 8 hours, cooled and evaporated. The white powder was analysed by titration (0.1N HCl). Found (%): Na, 5.74. Calculated (%): Na, 6.42.

3,3-dimethyl-1,1,1-tris(γ-trifluoropropyl)disiloxane(2). To a solution of $HSi(CH_3)_2Cl$ (15.4 mL, 0.16mol) in toluene (40mL) was added dropwise a solution of tris(γ-trifluoropropyl)silanolate sodium in toluene (187mL, (%)Na-2.29) and pyridine (19.6 g, 0.25 mol). The reaction mixture was boiled 4 hours To the mixture was then added MTBE (500mL) and mixture was washed by several portions of deionized water. The organic layer was dried over sodium sulfate and evaporated. The crude product was purified by distillation at 73 ^{0}C/1.2 mmHg. Yield: 31.0 g (70%).

Dimethyl(pentafluorobenzyl)silane(3). To a magnesium turnings (2.24g, 0.092 mol) was added dropwise a solution of 1-(chloromethyl)-pentafluoroben-zene (10.00g, 0.046 mol), $HSi(CH_3)_2Cl$ (10.3 mL, 0.092 mol) in THF (50mL).The reaction mixture was heated at 65 ^{0}C over 4 hours. The mixture was then hydrolyzed with saturated solution of NH_4Cl, (600mL) of MTBE was added and mixture was washed by several portions of deionized water. The organic layer was dried over sodium sulfate and evaporated. The crude product was purified by column chromatography (silicagel) eluting with 2:1 $CHCl_3$/hexane. Yield: 8.6 g (77 %).

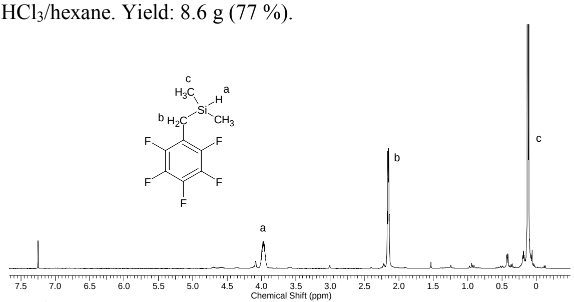


Figure 1. ^1H NMR spectrum of dimethyl(pentafluorobenzyl)silane in $CDCl_3$.

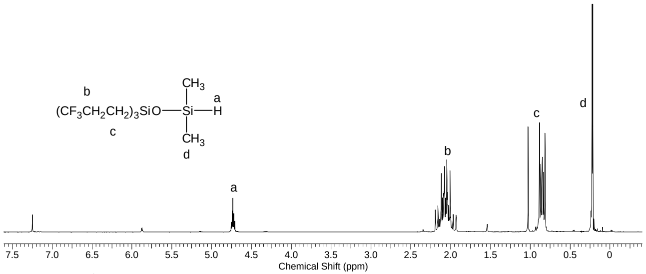


Figure 2. ^1H NMR spectrum of 3,3-dimethyl-1,1,1-tris(γ-trifluoropropyl) disi- loxane in $CDCl_3$.

Modification HbPACS by:

Dimethyl(pentafluorobenzyl)silane(4). To a solution of **HbPACS** (1.4708 g, 0.0116 mol) in MTBE (5mL) was added Pt-DVTMDS (10 mkL). After 10 min dimethyl(pentafluorobenzyl)silane (3.9 g, 0.01624mol) was added and reaction mixture was heated at 50 ^{0}C over 48 hours.

3,3-dimethyl-1,1,1-tris(γ-trifluoropropyl)disiloxane(5). To a solution of **HbPACS** (0.53 g, 0.0042 mol) was added Pt-DVTMDS (8 mkL). After 10 min 3,3-dimethyl-1,1,1-tris(γ-trifluoropropyl)disiloxane (3.5 g, 0.0067mol) was added and reaction mixture was heated at 110 ^{0}C over 72 hours. The reaction mixture was then cooled and dissolved in THF. The polymer was precipitated in ethanol and dried under vacuum. Yield: 1.93g (89%).

Chloro(dimethyl)silane(6). To a solution of **HbPACS** (5.00g, 0.0039 mol) was added Pt-DVTMDS (11 mkL). After 10 min $HSi(CH_3)_2Cl$ (7.5 g, 0.0078 mol) was added and reaction mixture was stirred at room temperature over 96 hours. The reaction mixture was then evaporated.

Tris(γ-trifluoropropyl)silanolate sodium(7). To a tris(γ-trifluoropropyl) silanolate sodium (4.2 g, 0.012 mol) was added pyridine (0.09 g, 0.0012 mol) and modified **HbPACS** by $HSi(CH_3)_2Cl$ (2.0 g, 0.009 mol).The reaction mixture was stirred over 24 hours. $(CH_3)_3SiCl$ was then added (1.28 g, 0.012 mol) and reaction mixture was stirred with heated at 60 ^{0}C over 3 hours. After the mixture was cooled, filtered and evaporated. The powder was dissolved in acetone(20mL), precipitated in ethanol (70mL) and dried under vacuum.

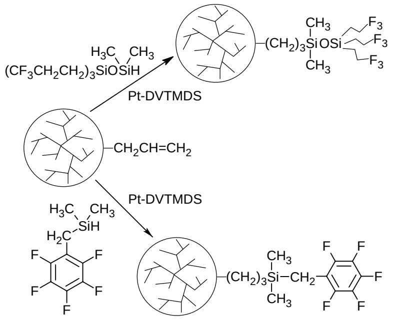
1-(chloromethyl)-pentafluorobenzene(8). To a magnesium turnings (1.8g, 0.075 mol) was added dropwise a solution of modified **HbPACS** by $HSi(CH_3)_2Cl$ (3.596 g, 0.01625 mol) and 1-(chloromethyl)-pentafluorobenzene (8.1g, 0.037 mol) in THF. The reaction mixture was heated at 65 ^{0}C over 6 hours. The mixture was then treated with methanol, filtered and evaporated.

Results and Discussion

The fluorocontaining modifiers. The synthesis of tris(γ-triftropropyl) sodium silanolate (1) was performed as siloxane bond cleavage in corresponding disiloxane compound by solution of sodium hydroxide in methanol. After water and methanol removing by azeotropic distillation with toluene the solution of targeting salt could be used directly in further reaction. The peculiar point of this compound it's good solubility in toluene unlike insolubility of starting hexakis (**γ**-trifluoropropyl)disiloxane and traditional poor solubility of sodium trimethylsilanolate. As it will be shown below (1) used for the modification in two stage method. For the one stage approach the corresponding tris(γ-triftropropyl)siloxydimethylhydrosililane was synthesized by interaction of (1) with dimethylchlorosilane and following distillation.

Another couple of modifiers for one stage and two stages modification approaches based on pentafluorobenzylchloride were prepared. First was simply Grignard reagent preparation and second it's transformation to corresponding hydridsilane as it depickted on scheme:

The HbPACS modification – one stage process. The scheme of two reactions shown below (Scheme 1). The similar hydrosilylation reactions in presence of Karsted catalyst were used in both cases. The conversion was readily monitored by ^{1}H NMR spectra. Even kinetic measurements did not performed significant differences between compound (2) and compound (3) could be mentioned. The modifier with aromatic part was much slower in reaction. Nevertheless in both cases full conversion of allylic groups was achieved



Scheme 1. The **HbPACS** modification – one stage process

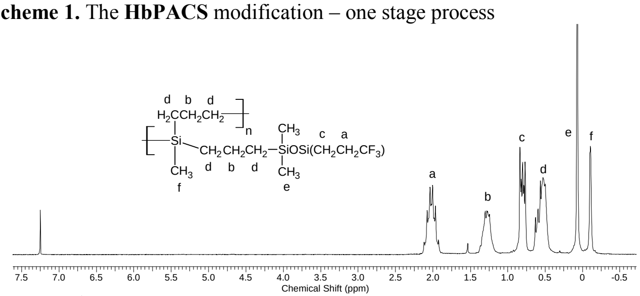
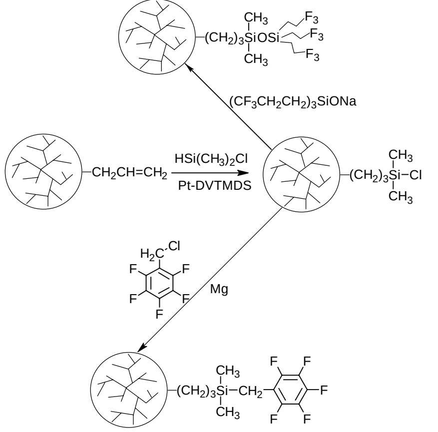


Figure 3. ^{1}H NMR spectrum of modification hyperbranched polycarbosilanes by 3,3-dimethyl-1,1,1-tris(γ-trifluoropropyl) disiloxane in $CDCl_3$.

The two stages approach was tested in both cases. The first stage hydrosilylaltion of **(HbPACS)** by dimethylchlorosilane was performed without any problem. Full conversion was achieved in according with data of ^{1}H NMR spectra. For the second stages two different reagents were used as it shown on Scheme 2. The reaction of chlorosilylderivatives of **(HbPACS)** (6) with (1) was ran in 10% excess of silanolate, which was terminated by trimethylchlorosilane after finishing of the reaction. The analysis of the product of reaction after precipitation and drying showed some amount of trimethylsiloxy groups in the ^{1}H NMR spectra. After analysis of mother solution of precipitation 3,3-dimethyl-1,1,1-tris(γ-trifluoropropyl)disiloxane was isolated and identified by GC analysis. The both factors demonstrated existence of side reaction during the interaction of (1) with (6). The nature of the side process concluded in cleavage of siloxane bond in polymer structure, which may lead to the formation of (7) and sodiumoxy-silyl group instead of tris(γ-trifluoropropyl)siloxy group. The process could lead to the intermolecular and intramolecular reactions with remaining chlorosilyl groups in polymer composition. The high molecular shoulder on GPC curve was detected. At the same time the analysis of prepared polymer showed that side process had negligible effect on the product structure. No crosslinked polymer was detected and only small deviations in polymer composition could be detected, which means that the second approach could be also used for the fluorinated derivatives preparation but with some additional care after side reaction. In case pentafluorobenzyl derivative in Grignard reaction side process was predictable. The Wurtz process was a major reaction during the Grinard reagent preparation stage by interaction of pentafluorobezylchloride with magnesium in THF solution. That is why the Grignard reagent preparation stage was combined with final stage the interaction with chlorosilyl- derivatives of **(HbPACS)**. Even in this case double excess of the Grignard reagent was used. Full conversion of the chlorosilyl groups was achieved. The results of the two approaches comparison for the fluoroaromatic derivatives of **(HbPACS)** will be discussed during the poster presentation since recently prepared sample still under study.



Scheme 2. The **HbPACS** modification – two stage process

Conclusion.

The synthetic schemes for the fluoro-containing derivatives of **HbPACS - (F-HbPACS)** were developed and tested. For the aliphatic variant of **F-HbPACS** both schemes showed acceptable results which led to isolation of target polymer with high yield. Because some side reaction in two step approach – one stage reaction was found as better way. Prepared polymer with high content of fluorine in composition is transparent colorless viscous liquid readily soluble in most of organic solvent which allows to investigate the organization of polymer globule depends onto solvent quality. The matter of special interest was study of solubility of prepared polymer in sc CO_2 in comparison with the fluorinated dendrimers[5] of similar chemical composition and molecular mass value.

The same directions of study planned for the fluoroaromatic derivatives of **HbPACS.** The similar synthetic procedures as for aliphatic analog faced with slower activity of the modifier in hydrosilylation process. In two steps scheme the Wurtz reaction as side process makes preparation of the target polymers more complex especially during isolation stage.

Thus, the performed experiments allow to make comparison of two different fluoroderivatives of the same polymer matrix in number of physico-chemical parameters.

References

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