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End-Functionalized Polymers. 1. Synthesis and Characterization of Perfluoroalkyl-Terminated Polymers via Chorosilane Derivatives

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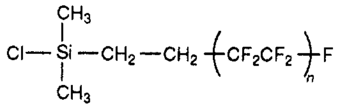
ABSTRACT: Surface-active, perfluoroalkyl-terminated block copolymers were synthesized and characterized. These heterophase block copolymers were made by terminating a variety of living anionic polymerizations with a chlorosilane derivative containing a perfluoroalkyl group. This synthetic methodology was successfully applied to the anionic polymerization of styrene and 1,3-dienes. Perfluoroalkyl-terminated poly(olefin)s were obtained via hydrogenation of the unsaturated poly(diene) materials. Excellent control of the molar mass, molar mass distribution, and functionality was verified using conventional characterization techniques such as gel permeation chromatography, NMR, and elemental analysis. In addition, time-of-flight secondary ion mass spectrometry (TOF-SIMS) was employed to characterize the absolute molar masses and molar mass distributions and also the extent of functionalization.

Introduction

Fluoropolymers have proven to be a very interesting and useful class of materials due to their unique balance of properties—low surface free energy, low coefficient of friction, nonflammability, low dielectric constant, and solvent and chemical resistance.[1] There are many classes of fluoropolymers covering a wide range of physical characteristics that include fluoroelastomers, protective poly(perfluoroalkyl acrylate) coatings, melt processible fluoroplastics, and poly(tetrafluoroethylene) (PTFE) to name a few. Perfluorinated polymers are virtually insoluble in all organic solvents and are resistant to very corrosive chemicals. For example, PTFE is attacked only by fluorine at elevated temperatures, chlorotrifluoromethane, and molten alkali metals.[2] Fluoroelastomers are very thermally stable and can exhibit low gas permeability.[3] These properties have been extensively exploited in high temperature sealing applications in contact with hydrocarbons and oils. PTFE is the highest volume and most widely recognized fluoropolymer. Since its discovery in 1938, it has revolutionized many plastics applications. PTFE has found extensive use as powdered lubricants for engine parts, seals, and pistons rings, cable coatings, membranes (Gore-Tex), weather resistant surface coatings, etc. However, due to their unique properties, fluoropolymers are inherently difficult to synthesize and process. The synthesis of these polymers usually involves high temperature and pressure in the gas phase, suspension, or emulsion polymerizations. Similarly, the processing of these materials requires high temperatures and may involve the evolution of corrosive and/or toxic chemicals, such as hydrogen fluoride. In order to circumvent the difficulties and expense associated with producing new fluoropolymers for various applications, fluorine-containing additives have been used to modify the surface properties of hydrocarbon polymers, such as poly(vinyl chloride), poly(acrylamide), and poly(methyl methacrylate). It has been shown that small amounts (0.2–1.0%) of these fluorocarbon additives significantly reduce the surface energy of the hydrocarbon polymer.[4] However, the utility of these additives is limited by the incompatibility of fluorocarbons with hydrocarbons.[5,6] To circumvent some of these problems, we became interested in the synthesis of heterophase block copolymers composed of fluorinated segments attached to conventional polymers such as poly(styrene), poly(diene)s, and poly(olefin)s, etc. Our initial efforts are focused on the use of functionalization methods to achieve these goals.

The terminal functionalization of living anionic polymerizations has been an active area of study.[7-14] These terminal functional groups include carboxylic acids, sulfonates, amines, hydroxyls, and silanes. It is the focus of the research reported herein to explore the synthesis and characterization of novel poly(tetrafluoroethylene) (PTFE) end-capped materials via nucleophilic substitution of perfluoroalkylchlorosilanes



$$\mathrm{Cl-Si(CH_3)_2-CH_2-CH_2-(CF_2CF_2)_{n}-F}$$

using living polymeric carbanions. An extensive on-line structural search of fluorinated chlorosilanes and siloxanes gave over 90 cited references, many very recent. Most of the work focused on the functionalization of surfaces to impart water repellency or lubricity. A perfluoroalkylated initiating species was used to make poly(dimethylsiloxane) for use as a waterproofing agent.[15] Similarly, perfluoroalkylsilylamines were used to treat SiO_2–ZrO_2-coated polycarbonate lenses.[16] Perfluoroalkylchlorosilanes have also been used as coatings to increase water, oil, and abrasion resistance of poly(methyl methacrylate).[17] The perfluoroalkylchlorosilanes have also been used in the synthesis of surfactants; however, no report discussed their use in the direct termination of living anionic polymerizations.[18-24]

The functionalized polymers in this study have been characterized by time-of-flight secondary ion mass spectrometry (TOF-SIMS). Traditional methods of end-group characterization offer only indirect data on the extent of functionalization. Because perfluoroalkyl groups are chemically inert, there are no titration methods which could be used to determine the extent of functionalization. Elemental analysis gives approximate information on the extent of functionalization via the atomic weight percent of fluorine. Even for low molar mass samples, GPC gives only qualitative termination data by determining the change in molar mass between the end-group-terminated

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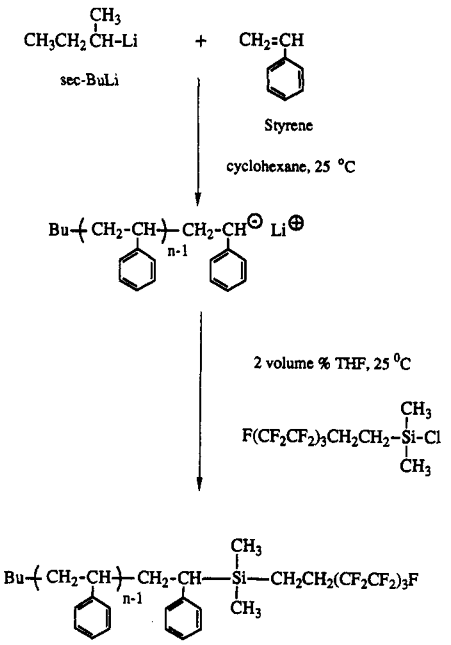
Scheme I



polymer and the polymer aliquot taken prior to termination. This molar mass shift cannot be used to quantitatively determine the extent of functionalization and offers no information on the chemical nature of the end group. Various mass spectrometric studies have allowed structural characterization of polymeric materials. Pyrolysis GC-MS[25,26] and quadrupole SIMS[27] studies have given information only on end groups and repeat unit fragments. Field desorption[28] and laser desorption mass spectrometry[29,30,31] have given information on end groups and repeat unit fragments in high molar mass polymers and intact polymer distributions for low molar mass polymers. Matrix-assisted laser desorption (MALD) has given molar mass information for high molar mass polymers.[32,33] Benninghoven has pioneered the characterization of low molar mass polymers (solution deposited as monolayers on solid substrates such as silver) using TOF-SIMS.[34] Here, TOF-SIMS is employed, not only to characterize molar mass and structure but also to evaluate the extent to which the polymers have been terminated with perfluoroalkylsilyl end groups. We demonstrate the power of TOF-SIMS in its ability to determine molar mass (in good agreement with GPC) as well as to characterize the structure and extent of functionalization of the polymers. End-group characterization via TOF-SIMS is especially advantageous, since traditional methods allow only indirect evaluation.

Experimental Section

Reagents. Cyclohexane (Phillips Petroleum) was stirred over concentrated sulfuric acid for ca. 2 weeks, decanted, and distilled under argon from sodium metal. Tetrahydrofuran (Fisher, Certified Grade) was distilled under argon from the purple sodium benzophenone ketyl. Styrene (Fisher, Certified Grade), isoprene (Goodyear Tire and Rubber), and butadiene (Phillips Petroleum) were vacuum distilled from dibutylmagnesium (Lithco) following three freeze–thaw cycles. The initiator, *sec*-butyllithium (Lithco), was used as received, and the molar concentration was determined by the Gilman double titration method.[35] The particular perfluoroalkylchlorosilane used in this initial study was (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-dimethylchlorosilane (Petrarch) and was used as received. The anionic polymerization was conducted in a one-neck 500-mL, round-bottomed flask equipped with a magnetic stir bar and rubber septum under a 6–8 psig argon atmosphere.

Table I. Molar Mass Data for the Perfluoroalkyl-Terminated Polymers with the Corresponding Aliquots[a,b]

sample	target $\langle M_n \rangle$ (g/mol)	$\langle M_n \rangle$ ($\times 10^{-3}$) (g/mol)	$\langle M_w \rangle / \langle M_n \rangle$
PS	1K	0.99	1.10
PS-*b*-PTFE		1.49	1.07
	5K	4.34	1.06
		4.76	1.05
	40K	41.8	1.08
		42.9	1.08
PI[a]	1K	0.97	1.12
PI-*b*-PTFE[a]		1.28	1.08
	5K	4.68	1.06
		5.15	1.06
	20K	21.0	1.07
		22.3	1.07
	40K	39.0	1.09
		41.9	1.10
PBD[a]	1K	0.92	1.11
PBD-*b*-PTFE[a]		1.22	1.08
	5K	5.13	1.18
		5.33	1.18

[a] PI and PBD molar masses normalized from PS standards. [b] Molar mass of silane end group = 406 g/mol.

Synthesis of Poly(styrene)–$Si(CH_3)_2CH_2CH_2C_6F_{13}$. Polymers were made having molar masses that ranged from 1K g/mol to 40K g/mol. The synthesis of a 1K g/mol sample was conducted as follows. The flask was charged with 11.0 mL (10.0 g) of styrene in ca. 100 mL of dry cyclohexane. The polymerization was initiated by the addition of 7.26 mL of a 1.38 M solution of *sec*-butyllithium in cyclohexane. The resulting orange-red solution was allowed to stir for ca. 2 h, after which ca. 2 mL of dry tetrahydrofuran was added to the solution. The polymerization was functionally terminated with the addition of 6.62 mL of (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-dimethylchlorosilane (20% excess) via syringe and was allowed to stir for ca. 30 min. During this time the solution became cloudy due to the precipitation of lithium chloride. The polymer from the reaction with a target molar mass of 1K g/mol was isolated by simple rotary evaporation, redissolved in dichloromethane, and washed with water. The dichloromethane solution was then rotary evaporated to dryness. The polymers with higher molar masses were precipitated directly into a 10-fold excess of methanol and washed several times with methanol and water. All of the polymers were dried under reduced pressure at 40 °C for 12 h.

Synthesis of Poly(isoprene)–$Si(CH_3)_2CH_2CH_2C_6F_{13}$. The poly(isoprene) analogs of the functionalized poly(styrene) system were prepared in a fashion similar to that detailed above; however, all of the polymers were isolated in the same manner as the $\langle M_n \rangle$ = 1K g/mol poly(styrene).

Synthesis of Poly(butadiene)–$Si(CH_3)_2CH_2CH_2C_6F_{13}$. The synthesis of a 1K g/mol poly(butadiene) was conducted as follows. The flask, while immersed in an acetone–crushed ice–sodium chloride bath, was charged with 15.5 mL (10.0 g) of butadiene in ca. 100 mL of dry toluene. Toluene (mp = −93 °C) was used as the solvent rather than cyclohexane (mp = 6 °C) due to the low temperature used to condense butadiene (bp = −4.5 °C). The polymerization was initiated by the addition of 7.26 mL of a 1.38 M solution of *sec*-butyllithium in cyclohexane. The resulting light yellow solution was then allowed to stir for 12 h, after which 2 mL of dry tetrahydrofuran was added to the solution, resulting in a very bright greenish-yellow color. To functionally terminate the polymerization, 6.62 mL of (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-dimethylchlorosilane (20% excess) was added via syringe and allowed to stir for ca. 30 minutes. During this time, the solution became cloudy with the precipitation of lithium chloride. The polymer (at all molar masses) was worked up in the same manner as the $\langle M_n \rangle$ = 1K g/mol poly(styrene).

Hydrogenation of Poly(diene)–$Si(CH_3)_2CH_2CH_2C_6F_{13}$ Materials. The poly(diene) (ca. 2 g, $\langle M_n \rangle$ = 1K g/mol) was dissolved

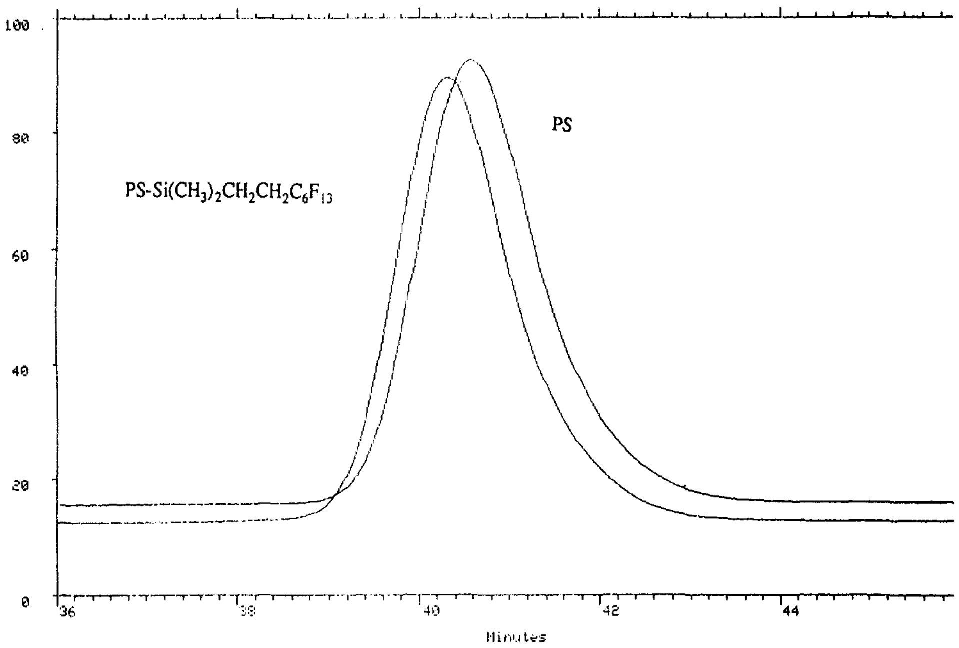


Figure 1. GPC overlay plot of $\langle M_n \rangle$ = 5K g/mol PS-*b*-PTFE and PS aliquot.

in 200 mL of dry cyclohexane. To this solution was added ca. 0.3 g of 10% Pd/C and the slurry was transferred into a medium pressure reactor.[36] The reactor was pressurized to ca. 50 psig with hydrogen gas and the solution was kept at 50 °C for 12 h and vigorously agitated. The slurry was filtered through Celite, sand, and filter paper to remove the palladium catalyst. The filtrate was rotary evaporated to recover the hydrogenated poly(diene) and dried at reduced pressure for 12 h.

Gel Permeation Chromatography and Elemental Analysis. A Waters 150-CV gel permeation chromatograph with Ultrastyragel columns of 100-, 500-, 10^3-, 10^4-, and 10^5-Å porosities in tetrahydrofuran was used with poly(styrene) standards (Showa Denko) for the determination of molar mass and molar mass distribution. Elemental analysis (CHF) was performed by Galbraith Laboratories, Inc.

X-ray Photoelectron Spectroscopy (XPS). Surface analysis of the PS-*b*-PTFE polymer was performed using a Perkin-Elmer Physical Electronics Model 5400 X-ray photoelectron spectrometer, with a base pressure of 5×10^{-10} Torr, using a Mg Kα anode at 400 W and 15 kV. Samples were prepared by spin casting a 20% w/v solution of polymer in chloroform onto 1 mm^2 Si at 6000 RPM for 1 min. Fluorine sampling depths (depth = $3\lambda \sin \theta$) were calculated for amorphous poly(styrene) at angles (θ) of 20, 40, and 70°. The inelastic mean free path (λ) was determined for organic compounds according to Seah and Dench.[37] XPS results are given as weight percent to allow direct comparison with other forms of analysis. The atomic percent fluorine was calculated using relative sensitivity factors from ref 38. Conversion to weight percent was based on theoretical calculations for 1K g/mol poly(styrene).

Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS). The TOF-SIMS spectra were acquired using the TOF-II reflection instrument developed and located at the University of Münster.[39] Typical instrumental conditions during TOF-II spectrum acquisition were 1.2-pA primary Ar$^+$ current, 200-s acquisition times, 0.25 mm^2 analysis area, and 10-keV post-acceleration. Primary ion doses were approximately 1×10^{12} ions/cm^2. Samples were prepared by depositing 1 μL of polymer solution in chloroform (1 mg/mL) onto about 80 mm^2 of an etched silver substrate (monolayer preparation).

Results and Discussion

Synthesis and Molecular Characterization. The preparation of the perfluorinated functional materials with 100% functionality, controlled molar mass, and narrow molar mass distribution was the main focus of this study. In order to meet these synthetic criteria, living anionic polymerization techniques were used in conjunction with the fluorinated alkylchlorosilane derivatives. The fluoroalkylchlorosilane terminating reagent and analogs with different fluorinated chain lengths can be conveniently synthesized from the corresponding perfluoroalkyl iodide.[40-42]

Table II. Elemental Analysis of the Perfluoroalkyl-Terminated Polymers

sample	target $\langle M_n \rangle$	wt % F calcd	wt % F found
PS-*b*-PTFE	1K	17.58	16.37
	5K	4.59	7.26
	40K	0.61	0.61
PI-*b*-PTFE	1K	17.58	14.30
	5K	4.53	3.99
	20K	1.21	0.88
	40K	0.61	0.11
PEP-*b*-PTFE	1K	17.22	12.28
PBD-*b*-PTFE	1K	17.58	16.86
	5K	4.53	1.81
LLDPE-*b*-PTFE	1K	17.13	14.56

Living polymerization gives unparalleled control of the molar mass of the polymer simply by controlling the ratio of monomer to initiator. The living nature of the chain end refers to the absence of termination and chain-transfer reactions and therefore allows for the synthesis of functionalized polymers. Block copolymerization is limited by the reactivity (pK_a) of the second monomer relative to the nucleophilicity of the first block chain end. Thus, there are limitations on the order of addition for the synthesis of block copolymers and to the types of block copolymer compositions that can be achieved. However, by the utilization of functionalization methods many different end groups, including perfluoroalkyl groups, may be attached to the polymer chain end quantitatively. The quantitative functionalization and molar mass control make living anionic polymerization ideal for this application. Living anionic polymerizations are applicable to a wide range of monomers including styrenics, 1,3-dienes, siloxanes, and alkyl methacrylates. The styrenics and dienes have been widely studied and yield very good results under standard conditions; thus, these hydrocarbon systems were chosen for our initial studies.

The anionic polymerization of styrene with subsequent termination using the perfluoroalkylchlorosilane is outlined in Scheme I. THF was added to the reactions in order to loosen the ion pair and to break up aggregation of the ion pairs to facilitate nucleophilic displacement of the chlorosilane. It was found that displacement of the chloride was extremely slow (no LiCl precipitation over several hours) without addition of THF. As shown in Table I, there is very good agreement between the target molar masses and the experimentally obtained molar masses for the PS-*b*-PTFE samples. Figure 1 is an overlay of the gel permeation chromatograms of the 5K g/mol PS prior to termination and the functionally terminated sample which illustrates the shift in molar mass between the proton terminated aliquot and the perfluoroalkyl-terminated polymer. The difference in molar mass determined by GPC corresponds well to the molar mass of the terminating fragment (406 g/mol). Similarly, poly(isoprene) (target $\langle M_n \rangle$ = 1K, 5K, 20K, and 40K g/mol) and poly(butadiene) (target $\langle M_n \rangle$ = 1K and 5K g/mol) were terminated with the perfluoroalkylchlorosilane following addition of THF. As shown in Table I, there is again very good agreement between the target molar masses and the experimentally determined number average molar mass values. The molar masses as determined by GPC for PI-*b*-PTFE and PBD-*b*-PTFE were normalized from poly(styrene) standards using constants of 1.35 and 1.75, respectively.[43]

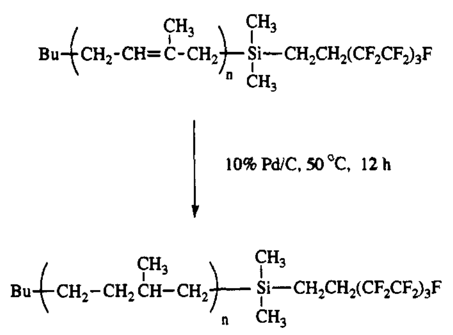
In all cases (PS, PI, and PBD) there is reasonably good agreement between the calculated fluorine weight percent and the actual value determined by elemental analysis at all molar masses (Table II), which demonstrates the excellent control of the molar mass, molar mass distribution, and functionality *using conventional characterization techniques*.

Hydrogenation of PI-*b*-PTFE and PBD-*b*-PTFE ($\langle M_n \rangle$ = 1000). The hydrogenation of the poly(diene)-*b*-PTFE polymers, outlined in Scheme II, affords poly(olefin) polymers with the perfluorinated chain ends. Due to the poly(olefin) structure of these materials, the potential miscibility with poly(olefins)s such as poly(ethylene) and poly(propylene) may give rise to important future blending applications utilizing the low surface energy properties of the perfluorinated segment. We will denote the hydrogenated PBD-*b*-PTFE as LLDPE-*b*-PTFE, because the hydrogenated poly(butadiene) contains short chain branches, similar to linear, low-density polyethylene (LLDPE), as a result of the 1,2-microstructure defects which occur during the anionic polymerization of 1,3-butadiene. Similarly, hydrogenated PI-*b*-PTFE will be denoted as PEP-*b*-PTFE (poly(ethylene-*alt*-propylene)-*b*-PTFE). The poly(isoprene) is ca. 90% *cis*-1,4-addition product when initiated with butyllithium in cyclohexane.[44] Comparison of the ^{1}H NMR spectra of PI-*b*-PTFE and PEP-*b*-PTFE and of PBD-*b*-PTFE and LLDPE-*b*-PTFE shows the disappearance of the olefinic protons following hydrogenation. The hydrogenated samples were extracted with methanol in order to remove any fluorinated segments which may have been cleaved during hydrogenation. The stability of the perfluoroalkylsilyl end group to catalytic hydrogenation was verified by the presence of the chemical shifts due to the silylmethyl protons (δ = 0 ppm) in the spectra of PEP-*b*-PTFE and LLDPE-*b*-PTFE, indicating PS–Si junction point stability. Elemental analysis of the PEP-*b*-PTFE and LLDPE-*b*-PTFE (Table II) confirms the presence of fluorine in both cases.

TOF-SIMS Characterization. The above GPC and elemental analyses all present strong evidence for the success of the syntheses of the perfluoroalkyl-terminated polymers. The structure of the polymers can be unequivocally confirmed, however, using time-of-flight secondary ion mass spectrometry (TOF-SIMS), with which signals are generated that correspond to intact polymer chains at each degree of polymerization. The TOF-SIMS spectrum of perfluoroalkyl-terminated poly(styrene) ($\langle M_n \rangle$ = 1K g/mol), shown in Figure 2, illustrates the utility of TOF-SIMS for the characterization of macromolecules. The most intense series of signals corresponds to the mass of an intact poly(styrene) chain of a specific degree of polymerization (*n*), which includes the mass of the *sec*-butyl initiator, *n* repeat units, the perfluoroalkylsilyl end group, and a silver atom (which aids in the ionization process). The distance between each of the signals is equal to the mass of the repeat unit, in this case 104 g/mol. The high resolution of TOF-SIMS is illustrated by the presence of several isotopic peaks corresponding to a specific degree of polymerization (Figure 3). Each set of peaks corresponds to the intact polymer chain with end group having a convolution of isotopic distributions of C, Ag, and H. For example, predominant contributors to the five main peaks in Figure 3 are as follows: Peak 1 corresponds to the polymer chain with one ^{107}Ag isotope, while peak 3 is the polymer with one ^{109}Ag isotope. Contributions from the polymer chain with two ^{13}C isotopes and one ^{107}Ag are also incorporated in peak 3. Peak 2 corresponds to the polymer with one ^{13}C isotope in the polymer and one ^{107}Ag isotope. Peak 4 corresponds to the polymer with one ^{13}C isotope in the polymer and one ^{109}Ag isotope. Finally, peak 5 corresponds to two ^{13}C isotopes in the polymer and one ^{109}Ag isotope.

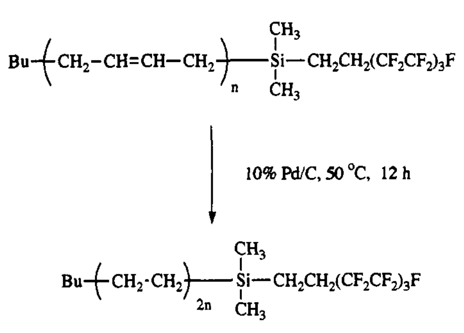
Scheme II

A) Poly(1,4-isoprene)-*b*-PTFE



poly(ethylene-*alt*-propylene)-*b*-PTFE

B) Poly(1,4-butadiene)-*b*-PTFE



LLDPE-*b*-PTFE

In short, the success of the synthesis of PS-*b*-PTFE is demonstrated by the presence of signals for intact polymer chains. Relatively weak signals are also observed for nonfunctionalized chains, accounting for chains that have

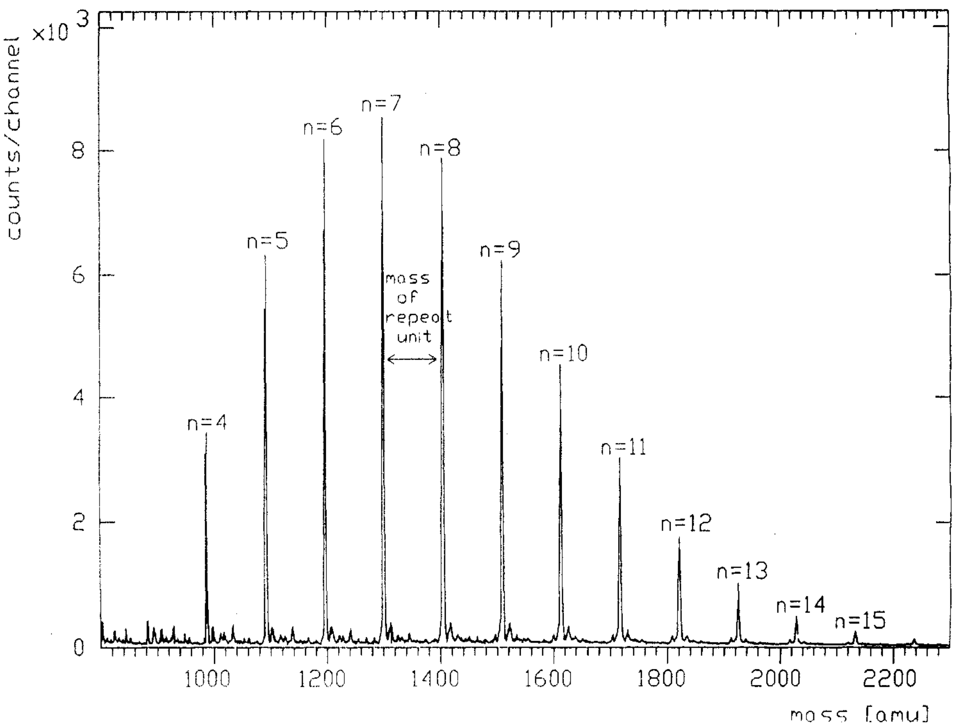


Figure 2. TOF-SIMS mass spectrum of $\langle M_n \rangle$ = 1K g/mol PS-*b*-PTFE.

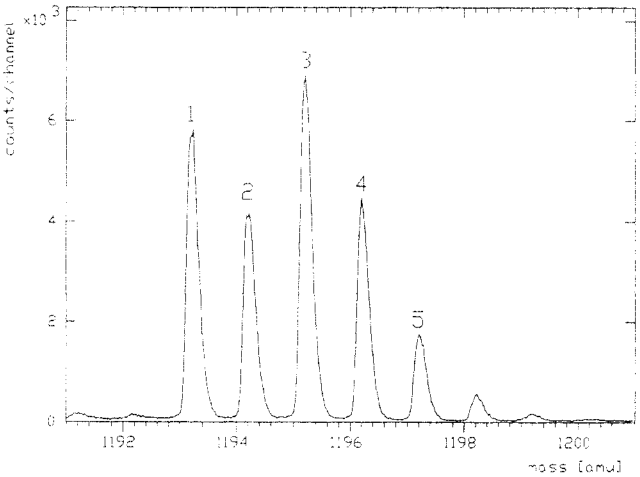


Figure 3. Identification of predominant contributors to TOF-SIMS multiple peaks due to C and Ag isotopes of PS-*b*-PTFE, n = 6 (Note: resolution < 1 amu): peak 1, PS-*b*-PTFE + ^{107}Ag; peak 2, PS-*b*-PTFE + ^{13}C + ^{107}Ag; peak 3, PS-*b*-PTFE + ^{109}Ag and PS-*b*-PTFE + ^{107}Ag + two ^{13}C in the polymer; peak 4, PS-*b*-PTFE + ^{13}C + ^{109}Ag; peak 5, PS-*b*-PTFE + ^{109}Ag + two ^{13}C in the polymer.

been terminated with a proton or that have become fragmented during ion bombardment. Presently, we are evaluating the potential of TOF-SIMS to quantify percent functionalization by accounting for differences in probability of sputtering, ionization, and detection. This being said, however, we find that the absolute molar masses determined by TOF-SIMS are in excellent agreement with the values determined by classical GPC techniques. Similar TOF-SIMS analyses have confirmed the structure and determined the molar masses of the perfluoroalkyl-terminated poly(isoprene) and poly(butadiene) analogues (Table III).

XPS Surface Analysis of PS-*b*-PTFE. Because PTFE has a low surface energy relative to PS, it was expected that the PTFE end group would dominate the air–polymer interface. Angle-dependent X-ray photoelectron spectroscopy (ADXPS) is a technique used to study composition of the surface of a material as a function of depth. In order to quantify the surface composition, ADXPS was performed at angles of 20, 40, and 70° on spun cast samples. The higher angles of analysis penetrate deeper into the surface and reflect the composition average of approximately the top 7, 4, and 2 nm at 70, 40, and 20°, respectively. ADXPS indicates that the quantity of fluorine is greater at the air–polymer interface than it is in the bulk. As the depth of sampling is increased, the fluorine content decreases, suggesting that the lower surface energy perfluorinated segment segregates to the surface at all molar masses (Table IV). The most dramatic illustration of the surface segregation is for the $\langle M_n \rangle$ = 40K g/mol sample. Although the bulk fluorine content by elemental analysis is only 0.37 wt %, the fluorine content at the surface is 2.81 wt %, giving an enhancement factor (surface content/bulk content) of 7.6.

Table III. Comparison of Molar Mass Data from GPC and TOF-SIMS of $\langle M_n \rangle$ = 1K g/mol Perfluoroalkyl-Terminated Polymers

	GPC		TOF-SIMS	
sample	$\langle M_n \rangle$ ($\times 10^{-3}$) (g/mol)	$\langle M_w \rangle / \langle M_n \rangle$	$\langle M_n \rangle$ ($\times 10^{-3}$) (g/mol)	$\langle M_w \rangle / \langle M_n \rangle$
PS-*b*-PTFE	1.37	1.08	1.30	1.03
PI-*b*-PTFE	1.28	1.08	1.35	1.04
PBD-*b*-PTFE	1.22	1.08	1.26	1.03

Table IV. ADXPS Surface Segregation Data of $\langle M_n \rangle$ = 1K, 5K, and 40K g/mol PS-*b*-PTFE

target	wt % F			XPS sample	enhancement
$\langle M_n \rangle$	calcd	found	XPS	depth (nm)	factor
1K	17.58	16.37	27.6	2	1.6
			18.8	4	
			13.2	7	
5K	4.59	5.40	13.2	2	2.4
			7.2	4	
			6.5	7	
40K	0.61	0.37	2.8	2	7.6
			1.9	4	
			1.6	7	

Conclusions

The termination of a living polymeric carbanion with a perfluorinated chlorosilane is a facile, one-pot synthesis of PTFE-functional materials. This synthetic methodology has been successfully applied to styrenics and dienes. PTFE-functional poly(olefin)s are easily synthesized via hydrogenation of the PTFE-functional poly(diene)s. These materials should prove to be useful surface modifiers for a wide range of commercially available thermoplastics. TOF-SIMS has proved to be a powerful technique for the characterization of the chemical structure of polymers not only for the determination of absolute molar masses and molar mass distributions but also for the direct verification of functionalization.

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