oxonium ion by 2-iodopropane to form an iodonium ion.[5] Attack of the iodonium at the methine carbon by THF or polymer results in the formation of iodide-terminated chain and initiates a new chain. The other mechanism (Scheme III) involves the decomposition of the SbF_6 ion to form a fluoride-terminated chain and SbF_5. The Lewis acid reacts with 2-iodopropane to generate a carbenium ion which subsequently initiates a new chain.

The SbF_6 ion is one of the most stable counterions used in cationic polymerization. The rate of its decomposition is not known in this type of system. Likewise the relative stabilities of iodonium and oxonium ions are not clear.[6] Presently we favor the first of the two mechanisms for the following reasons. The ^{19}F NMR spectrum of the polymer after 3 months did not exhibit any signals for an alkyl fluoride end group. Additionally one may expect that Scheme II would be independent of the halide concentration, since the reaction of SbF_5 with alkyl halides is known to be fast[7] and the decomposition of the counterion would be rate-determining.[8] Although strict temperature control was not maintained for the NMR sample, we calculated from the NMR and GPC data the apparent rate constants for the two rate laws:[9]

$$-d[C_3H_7I]/dt = k_{app}[(C_4H_8O)_n{}^+SbF_6{}^-][C_3H_7I]$$

$$-d[C_3H_7I]/dt = k_{app}[(C_4H_8O)_n{}^+SbF_6{}^-]$$

The NMR data indicated a pseudo-first-order rate constant of 3×10^{-7} s^{-1}, while the GPC data indicated that the rate constant should be 2×10^{-6} s^{-1}, a discrepancy of 1 order of magnitude. Assuming a pseudo-second-order rate law, both the NMR and GPC data yield rate constants of 5×10^{-6} L mol^{-1} s^{-1}.

In conclusion, rapid chain transfer to propionic acid chloride and slow chain transfer to 2-iodopropane in the polymerization of THF have been demonstrated. Such reactions permit the preparation of polymers with the molecular weight determined by chain transfer allowing for the use of only small amounts of silver salt. Additionally, this may be useful in systems where chain transfer to polymer is slow, for the preparation of asymmetrically substituted telechelic polymers and block and graft copolymers.

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Registry No. THF, 109-99-9; $AgSbF_6$, 26042-64-8; H_3CCH_2COCl, 79-03-8; $H_3C(CH_2)_2I$, 75-30-9.

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(4) A similar mixture of THF and propionic acid chloride without the silver salt showed no change for the same ratio of THF to acid chloride as in this experiment and no additional chemical species after 350 h by gas chromatographic analysis.
(5) This mechanism would be equivalent to the formation of a carbenium ion by iodide exchange with an oxonium ion. The iodonium ion intermediate seems more reasonable as the equilibrium constant for the reaction $R'-I + R^+ \rightarrow R'-I-R^+$ is probably large; see Sen Sharma et al. and Olah (Sen Sharma, D. K.; Menza de Holer, S.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 3757. Olah, G. A. *Halonium Ions*; Wiley: New York, 1975).
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(8) One might expect to observe autocatalysis with this mechanism as the SbF_5I^- ion is less stable than the SbF_6^- ion. No evidence for autocatalysis was seen in the ^1H NMR spectra.
(9) These are pseudo-second-order and pseudo-first-order expressions, as the concentration of THF and ether oxygen are at their equilibrium value before any chain transfer is observed.

Polymer Monolayers Prepared by the Spontaneous Adsorption of Sulfur-Functionalized Polystyrene on Gold Surfaces[1]

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ABSTRACT: Polystyrene containing one terminal thiol group (PS-SH) and styrene–propylene sulfide block copolymers (PS–PPS) were allowed to adsorb on evaporated gold films supported on glass. The resulting supported films were characterized by X-ray photoelectron spectroscopy, external reflectance infrared spectroscopy, and scintillation counting of radioisotope-labeled polymers. The polymers adsorb rapidly and irreversibly, and the polymer monolayers can be washed with fresh solvent without desorption. The effects of molecular weight, concentration, and solvent power on adsorbance were determined for PS-SH. The effect of propylene sulfide block size for a series of PS–PPS copolymers on the number of adsorbed chains was determined.

Introduction

The modification of surfaces by adsorption of polymer molecules is important to a range of technologies (for example, corrosion,[3] lubrication,[4] colloid stabilization[5]) where interfacial effects are dominant. This field of research has received considerable attention recently from both theoretical[6-8] and experimental[9-11] groups.

This paper describes the preparation of thin films of polystyrene on evaporated gold surfaces by adsorption of modified polystyrenes from solution. Two types of modified polymer were studied: polystyrene containing one terminal thiol group (PS-SH) and styrene–propylene

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sulfide block copolymers (PS–PPS). These systems were chosen because of their preparative ease and because of the high affinity of sulfur to gold[12–16] and allow spontaneous adsorption of polystyrene from good solvents, which unmodified polystyrene does not adsorb from. The broad objective of this research program is to control thin polymer film structure by adsorbing polymers containing high-affinity (for the substrate) functional groups in specific and controllable densities and locations on their chains. We report here the effects of molecular weight, concentration, solvent, and number of sites of attachment (propylene sulfide block size) on polymer adsorbance.

Experimental Section

Materials. Styrene (Fisher) and phenylacetylene (Aldrich) were distilled from calcium hydride at reduced pressure (20 mm) and stored under nitrogen at −20 °C. *n*-Butyllithium (2.5 M in hexane) and *sec*-butyllithium (1.6 M in hexane) were used as received from Aldrich and titrated with 4-biphenylmethanol[17] just prior to use. Propylene sulfide (Aldrich) was distilled from calcium hydride and stored under nitrogen. Benzene and THF were distilled from sodium benzophenone dianion and stored under nitrogen. Pentane was distilled from lithium aluminum hydride and stored under nitrogen. Lindlar's catalyst (5% palladium on calcium carbonate, poisoned with lead) was used as received from Aldrich. Tritiated water (1 mL, 100 mCi) (New England Nuclear) was diluted to 10 mL with doubly distilled water, degassed by repeated freeze–pump–thaw cycles, and stored under nitrogen. Gold (Alfa) was 99.999% pure. Corning glass cover slips (11 × 22 mm) and Fisherbrand glass microscope slides (25 × 50 mm) were rinsed with acetone, dried with a stream of nitrogen, washed with concentrated nitric acid, and dried under vacuum. Evaporated gold film substrates were prepared by using a Balzers MED 010 vapor deposition apparatus. Gold was evaporated from resistively heated tungsten baskets at a base pressure of 1×10^{-6} mm. Film thickness was controlled to ~1500 Å by monitoring the deposition with a quartz crystal thickness monitor. After deposition, the chamber was filled with prepurified nitrogen and the substrates were immediately placed in Schlenk tubes and stored under nitrogen.

Methods. X-ray photoelectron spectroscopy (XPS) was performed with a Perkin-Elmer Physical Electronics 5100 with Mg Kα excitation. Spectra were recorded at two angles: the film surface 15° and 75° from the analyzer. Atomic ratios were determined by using Physical Electronics software and programmed sensitivity factors. Samples charged variably and the reported binding energies are not corrected for charging. External reflectance infrared spectra (XR IR) were recorded by using p-polarized radiation reflected from the sample at an angle of incidence of 86° with a nitrogen-purged IBM-38 FT infrared spectrometer. Liquid scintillation counting (LSC) was performed by using a Beckman 3801 scintillation counter. The solid samples were submersed in OSC scintillation cocktail (Amersham). Beer's law plots of mass vs CPM were constructed for each polymer by using dilute solutions. To relate the scintillation results to the mass of the adsorbed polymer, the results were corrected for the 80% measured efficiency and doubled to account for sample geometry (the assumption being made that one-half of the β-particles reach the scintillant and one-half are absorbed by the gold or glass). Gel permeation chromatography (GPC) was carried out by using a Rainin Rabbit-HP pump, Polymer Laboratories 5-μm PL gel columns (10^2, 10^3, 10^4 Å), a Knauer refractive index detector, and an Apple IIe computer with IMI Chromatix GPC software. Molecular weights and distributions were determined relative to polystyrene molecular weight standards. Gas chromatography (GC) was performed with a Hewlett-Packard 5790A gas chromatograph, a Hewlett-Packard 3390A recorder–integrator, and a $^1/_8$ in. × 6 ft Analabs AN600 column. UV–vis analyses were performed with a Perkin-Elmer Lambda 3A spectrophotometer.

[β-^{3}H]Styrene. The reported synthesis of β-deuteriostyrene[18] was modified. A 250-mL pressure flask containing a magnetic stirring bar was purged with nitrogen and phenylacetylene (2.6 mL, 24 mmol) in 60 mL of pentane was introduced. *n*-Butyllithium (9.6 mL, 2.5M, 24 mmol) was added dropwise to the stirred solution. The reaction was quenched with [^{3}H]water (0.43 mL, 24 mmol, 10 mCi/mL). The [^{3}H]phenylacetylene solution was distilled (trap-to-trap) from the lithium salts and transferred to a 250-mL pressure flask containing a magnetic stirring bar and 0.35 g of Lindlar's catalyst. The flask was connected to a hydrogen manifold (22 psig), and the hydrogenation was allowed to proceed for 21 min. The solvent was removed at reduced pressure, and the [β-^{3}H]styrene was distilled trap-to-trap from calcium hydride.

Thiol-Terminated Polystyrenes (PS_x-SH).[19,20] A 50-mL Schlenk tube containing a magnetic stirring bar was purged with nitrogen, and 30 mL of benzene was added via cannula. Styrene (2.0 mL, 17.5 mmol) was added via syringe followed by the addition of the appropriate amount of initiator for the desired molecular weight. After the styrene was consumed (by GC), a small sample of the reaction mixture was removed, and from this sample the polymer was isolated and characterized by GPC. The polystyryl anions were titrated with propylene sulfide, and the polymers were protonated with acidic methanol and precipitated in methanol. Molecular weight data for all PS_x–SH samples are given in Table I. The subscript refers to the approximate degree of polymerization. Molecular weight data for the tritiated samples were obtained from cold samples prepared in side-by-side reactions.

Styrene–Propylene Sulfide Block Copolymers (PS_A–PPS_B).[19,20] Polystyryllithium was prepared and characterized as described above except THF was used as the solvent, and the reaction temperature was −78 °C. Propylene sulfide of the appropriate amount for the desired molecular weight was added, and the solution was allowed to warm to room temperature. The reaction was allowed to proceed until the propylene sulfide was consumed (by GC). The copolymers were protonated with acidic methanol and were isolated by precipitation in methanol. Molecular weight data for all PS_A–PPS_B copolymers are given in Table II; the data for the tritiated polymers were obtained from cold samples prepared in side-by-side reactions.

Polymer Adsorption. A gold film substrate was placed in a Schlenk tube which was then purged with nitrogen. Polymer solution (normally 2 mg/mL in THF) was introduced via cannula to cover the gold film substrate. After (normally) 24 h, the solution was removed via cannula and the substrate with adsorbed polymer was washed with fresh solvent until no polystyrene could be detected by UV–vis analysis of the washing solvent.

Table I
PS_x-H Characteristics

sample	M_n	M_w/M_n	CPM[a]
PS_{10}-SH	910	1.05	
PS_{50}-SH	5057	1.04	
PS_{100}-SH	9623	1.03	
PS_{600}-SH	57029	1.04	
PS_{1350}-SH	134729	1.06	
PS_{2000}-SH	203175	1.03	
PS_{5000}-SH	512558	1.08	
^{3}H-PS_{60}-SH	5544[b]	1.06[b]	784.9
^{3}H-PS_{180}-SH	17682[b]	1.06[b]	561.1
^{3}H-PS_{600}-SH	57970[b]	1.06[b]	516.1
^{3}H-PS_{2000}-SH	194993[b]	1.08[b]	287.2

[a] Counts per minute for 2.4×10^{-7} g in solution. [b] Determined from cold samples prepared in side-by-side polymerizations.

Table II
PS_A–PPS_B Characteristics

sample	M_n[a]	M_w/M_n[a]	CPM[b]
PS_{10}–PPS_{90}	60324	1.28	192.8
PS_{30}–PPS_{70}	61021	1.21	310.3
PS_{50}–PPS_{50}	58324	1.15	435.5
PS_{70}–PPS_{30}	59114	1.09	574.4
PS_{90}–PPS_1	57970	1.06	270.0

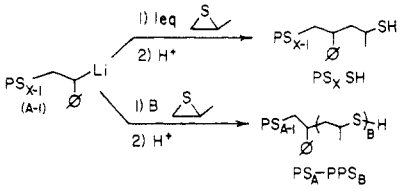
[a] Determined from cold samples prepared in side-by-side polymerizations. [b] Counts per minute for 2.4×10^{-7} g in solution.

Results and Discussion

Polymer monolayers were prepared by the adsorption of thiol-terminated polystyrenes (PS-SH) and styrene–propylene sulfide block copolymers (PS–PPS) from solu-

tion onto glass-supported evaporated gold films. The adsorption was followed, and the resulting monolayers were characterized by X-ray photoelectron spectroscopy (XPS), external reflectance infrared spectroscopy (XR IR), and liquid scintillation counting (LSC). We use the term "polymer monolayer" to mean a thin film of polymer in which each polymer molecule is attached to the surface; no order in the polymer film is implied. Most of the experiments that we discuss here were adsorptions from THF, a solvent from which unmodified polystyrene does not adsorb to gold.[21] PS-SH and PS–PPS monolayers are thus attached to the gold surface by gold–sulfur bonds. The gold substrates were prepared by thermal evaporation of ~1500 Å of 99.999% gold onto two types of glass: microscope slides (25 × 50 mm) were used for XR IR; microscope slide cover slips (11 × 22 mm) were used for XPS and LSC. The gold substrates were stored under nitrogen prior to use. XPS indicates that the surfaces of these substrates are contaminated by carbon-containing adsorbed impurities, however, most (if not all) of the impurities are displaced in the adsorption process.[22] The experiments that are discussed here were performed with the objective of determining what control over polymer film thickness could be exercised by changes in molecular weight, concentration, solvent composition and the number of sulfur atoms in the polymer chain.

Polymer Synthesis and Characterization. Tables I and II describe the molecular weight and polydispersity characteristics for PS_X-SH and PS_A–PPS_B samples, respectively. The subscript X indicates the approximate degree of polymerization of the thiol-terminated homopolymers and the subscripts A and B indicate the mole percent of styrene and propylene sulfide, respectively, in the block copolymers; each block copolymer has approximately the same total number of monomer units. The polymers were prepared by anionic polymerization of styrene followed by either end capping with 1 equiv of propylene sulfide (for PS_X-SH) or polymerization of a propylene sulfide block (for PS_A–PPS_B) (eq 1). All non-



(1a)

(1b)

radioactive polymers were analyzed by GPC; selected samples were analyzed by ^1H NMR, IR, and elemental analysis. Tritium-labeled polymers were prepared by using [β-^{3}H]styrene and were characterized only by LSC. Molecular weights of the labeled polymers were approximated by GPC of cold samples prepared in side-by-side polymerizations.

Adsorption Kinetics. We have not carefully determined the kinetics of adsorption but have determined conditions under which reproducible, steady-state polymer monolayers are formed. Adsorption experiments consisted of introducing polymer solutions (2 mg/mL in all experiments except the concentration studies which varied from 0.2 to 3 mg/mL) to Schlenk tubes under nitrogen via cannula to cover the glass-supported gold films. Exposure times varied from several minutes to several days. In all cases except the most dilute concentration studied, steady-state adsorbance was reached after 1 h (there was no difference between 1- and 24-h exposed samples by any analytical technique used). Adsorption from the most dilute solution (0.02 mg/mL) reached steady-state after 24 h. A plot of the LSC data for this adsorption experiment and another more representative experiment is shown in Figure 1. All other data reported in this paper were obtained from samples exposed to polymer solutions for 24 h.

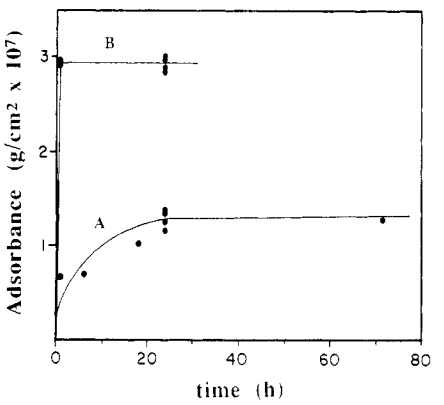


Figure 1. Time dependence of adsorbance for A, PS_{2000}-SH (0.02 mg/mL in THF), and B, PS_{2000}-SH (2.0 mg/mL in THF).

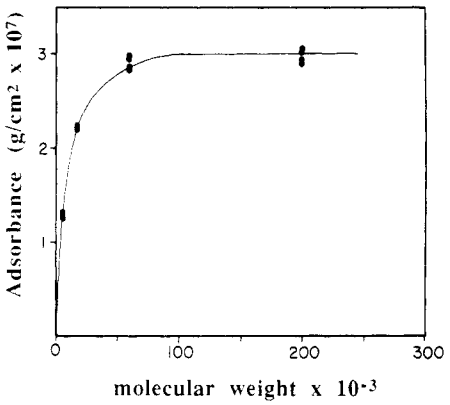


Figure 2. Adsorbance vs molecular weight for PS_X-SH determined by LSC.

Effect of Molecular Weight on Adsorbance. The amount of polymer adsorbed to gold substrates from THF solutions (2 mg/mL) was measured by two techniques (LSC and XPS) for PS_X-SH varying in molecular weight from 1000 (PS_{10}-SH) to 500 000 (PS_{5000}-SH). The highest molecular weight sample studied (PS_{5000}-SH) did not adsorb after 72 h. Evidently at a sufficiently high molecular weight (between 200 000 and 500 000), the sulfur–gold interaction is not sufficient to overcome the entropy loss and loss of polymer–solvent interactions incurred on adsorption and the thiol-terminated polystyrene behaves as though it were unmodified polystyrene. LSC was used to measure the mass of adsorbed polymer and was used to measure four samples of molecular weights 6000, 18 000, 60 000, and 200 000. The data are plotted in Figure 2. The data indicate that the quantity of adsorbed polymer increases rapidly with molecular weight in the low molecular weight regime and then levels. With the assumption that the dry polystyrene monolayer has the same density as bulk polystyrene (~1 g/cm^3), LSC data place the dry film thickness at ~13 Å for ^{3}H-PS_{60}-SH, ~22 Å for ^{3}H-PS_{18}-SH, and ~30 Å for ^{3}H-PS_{600}-SH and ^{3}H-PS_{2000}-SH. XPS was used to measure the ratio of carbon to gold in the outer 40 Å (75° takeoff angle—between the film surface and the analyzer). This method has significant error associated with it, and the results were somewhat scattered; however, they are in good agreement with the thicknesses calculated from the LSC data: PS_{50}-SH gave a C:Au ratio of 1.0 ± 0.3 (estimated thickness = ~15 Å). PS_{100}-SH, PS_{600}-SH, PS_{1350}-SH, and PS_{2000}-SH gave C:Au ratios of 1.9 ± 0.5, 2.2 ± 0.3, 2.5 ± 0.3, and 2.7 ± 0.5, respectively

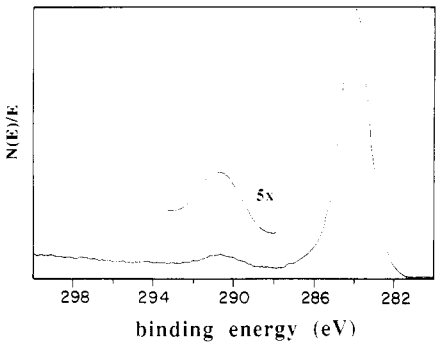


Figure 3. C_{1s} photoelectron spectrum (15° takeoff angle) P-S_{1350}-SH adsorbed to gold.

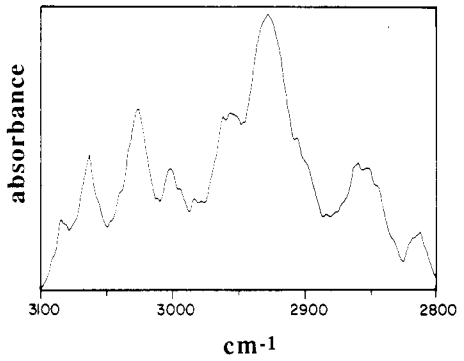


Figure 4. XR IR spectrum of PS_{100}-SH adsorbed to gold.

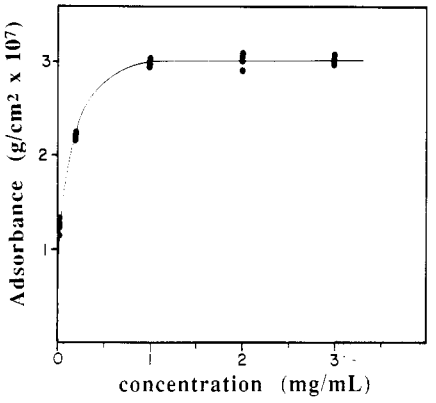


Figure 5. PS_{2000}-SH adsorption isotherm (THF solution).

(estimated thicknesses ~20–25 Å). It should be noted that these data yield average thicknesses and do not distinguish among a continuous film with a single thickness, a variably thick continuous film, and an island-like noncontinuous film. That the carbon observed by XPS is due to polystyrene is verified by the $\pi \rightarrow \pi^*$ shake-up satellite which is observed at 6.7-eV higher binding energy than the main C_{1s} photoelectron line (Figure 3). XR IR spectra of adsorbed thin films exhibit characteristic polystyrene absorbances due to C–H stretching (Figure 4) in the 3100–2800 cm^{-1} region, methylene bending (1493, 1453 cm^{-1}), and aromatic out-of-place bending (702 cm^{-1}). Gold film surfaces which had been exposed to PS_{5000}-SH exhibited neither polystyrene infrared absorbances nor a $\pi \rightarrow \pi^*$ shake-up satellite.

Effect of Concentration on Adsorbance. The adsorption isotherm for PS_{2000}-SH (from THF) is shown in Figure 5. The mass of polymer adsorbed at steady-state rises sharply from 0 to 0.2 mg/mL and levels above 1 mg/mL. This is typical behavior for polymers adsorbing to surfaces without a strong specific interaction, and this tendency indicates that at slower adsorption rates, the pendant polystyrene stretching into solution forms a polymer layer which inhibits adsorption of other chains.

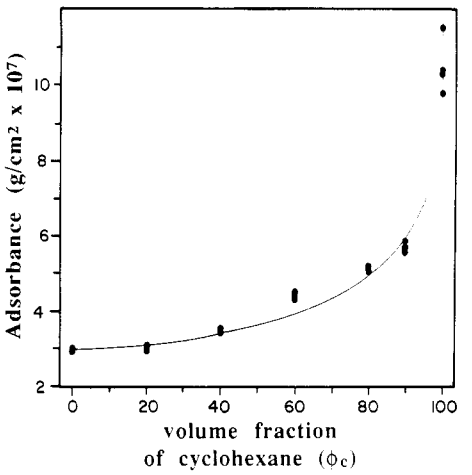


Figure 6. Solvent composition effect on adsorption from THF/cyclohexane mixtures.

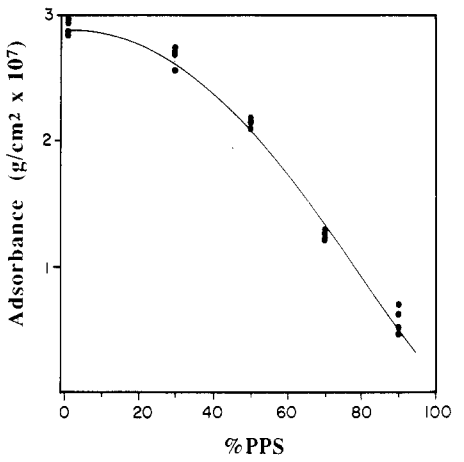


Figure 7. Effect of PPS block size on adsorbance of PS_A–PPS_B from THF solution.

This adsorption-inhibiting polymer layer also explains why the adsorbance levels off with molecular weight increase. If the chains adsorbed only at their termini and did not form an inpenetratable layer, there would not be a concentration dependence and the adsorbance would not level off with molecular weight increase. de Gennes has discussed the density profile of polymers attached to a surface by one end and in contact with a good solvent: he predicts that "blobs" will form and fill space densely in a layer close to the surface.[23]

Effect of Solvent Composition on Adsorbance. The adsorbance of PS_{200}-SH (2.0 mg/mL, 45 °C) on gold from a series of THF/cyclohexane mixtures was determined. Cyclohexane is a poor solvent for polystyrene at this temperature, and from it, unmodified polystyrene spontaneously adsorbs to gold. Adsorbance (determined by LSC) is plotted versus volume fraction of cyclohexane (ϕ_c) in Figure 6. The adsorbance gradually increases with increasing cyclohexane concentration. At $\phi_c = 1$ (neat cyclohexane) there is a large increase in the amount of polymer adsorbed. In a good solvent the polymer is more expanded and takes up more surface area, preventing other polymers from adsorbing. The nonlinearity of the data indicates preferential solvation of the polymer by THF. The same effect has been observed in solution for polystyrene in benzene/cyclohexane mixtures.[24,25]

Adsorption of Styrene–Propylene Sulfide Block Copolymers. A series of PS_A–PPS_B samples were prepared with B varying from 1 to 90% (Table II) and allowed to adsorb to gold from THF solution (2.0 mg/mL). Figure

7 shows the adsorbance results determined by LSC. The adsorbance decreases with increasing propylene sulfide block size. This is consistent with an adsorption in which the propylene sulfide block (the "sticky" part of the copolymer) strongly adheres and covers up the gold surface: The longer the propylene sulfide block, the fewer chains adsorb. This configuration was suggested[9] for styrene–2-vinylpyridine copolymers adsorbed on mica.

Conclusions

Polystyrene containing a terminal thiol group (PS_X-SH (M_n = 1000–200 000) adsorbs to gold under conditions that polystyrene does not. At higher molecular weight (M_n = 500 000) adsorption does not occur. Film thickness varies with molecular weight, concentration, and solvent property in a fashion similar to the way polystyrene film thickness varies when unmodified polystyrene adsorbs from a poor solvent. Styrene–propylene sulfide block copolymer (PS_A–PPS_B) samples adsorb to gold, and the thickness of the adsorbed polymer layer can be controlled by the length of the propylene sulfide block.

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Registry No. (S)(PS) (block copolymer), 113568-91-5; Au, 7440-57-5.

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Poly([1.1.1]propellane).[1] A Novel Rigid-Rod Polymer Obtained by Ring-Opening Polymerization Breaking a Carbon–Carbon σ-Bond

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ABSTRACT: Treatment of the [1.1.1]propellane **1** with lithium organic initiators such as *tert*-butyllithium and phenyllithium leads to anionically induced ring-opening polymerization of **1**. In the course of the polymerization only the central σ-bond in monomer **1** was opened, leading to an entirely new rigid-rod structure—the poly([1.1.1]propellane) **2**, whose degree of polymerization was determined to be greater than 20. The rigidity of polymer **2** is due to constraints inherently associated with its multicyclic structure. The structure of the poly([1.1.1]propellane) **2** was proved by means of solid-state NMR spectroscopy and was further confirmed by an investigation of soluble, oligomeric material having analogous constitution.

In the late sixties the first report of a ring-opening polymerization involving the central bond of a bicyclobutane derivative appeared in the patent literature.[2] In the following years this singular observation of breaking carbon–carbon σ-bonds in polymerization reactions has been developed to a fruitful field of research mainly by Hall and his co-workers.[3] They showed that, for several bicyclic systems, efficient polymerization occurs only if the strain in the monomer is sufficient to activate the bond in question. In the past few years small-ring propellanes have been established as a new class of highly strained organic molecules.[4] The most intriguing feature of their structures is bridgehead carbon atoms exhibiting "inverted geometry"[5] of the four substituents. This rather unusual bonding situation in propellanes has drawn the attention of both theoreticians and experimentalists toward electron distribution in, and reactivity of, such species.[4,6] The reactivity is reflected in that the central bond, though being a σ-bond formally, is highly prone to radical attack.[4,7] The question arises whether the reactivity of the central bond in small-ring propellanes is high enough to be utilized in ring-opening polymerization reactions. Such a polymerization would result in the formation of a new type of rigid polymer **2**, which is structurally completely different from

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