AD-A184 956 MOLECULAR-LEVEL SYNTHESIS AND CHARACTERIZATION OF METAL-POLYMER INTERFACE (U) MASSACHUSETTS UNIV AMHERST DEPT OF POLYMER SCIENCE AND ENGINE S L LING ET AL. 1/1

UNCLASSIFIED 23 AUG 87 ARO-20961.4-MS DAAG29-84-K-0052 F/G 7/6 NL

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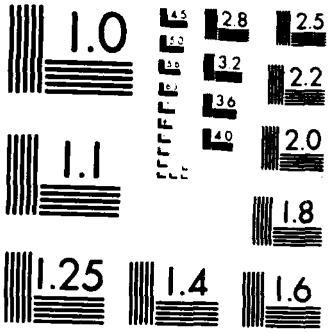

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Molecular-Level Synthesis and Characterization of Metal-Polymer Interfaces

Final Report

Shaw Ling Hsu and Thomas J. McCarthy

August 23, 1987

U.S. Army Research Office

DAAG 29-84-K-0052

Polymer Science and Engineering Department
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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION: Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT: Approved for public release; distribution unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S): ARP 20961.4-MS

6a. NAME OF PERFORMING ORGANIZATION: University of Massachusetts

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION: U. S. Army Research Office

6c. ADDRESS *(City, State, and ZIP Code)*
Amherst, MA 01003

7b. ADDRESS *(City, State, and ZIP Code)*
P. O. Box 12211
Research Triangle Park, NC 27709-2211

8a. NAME OF FUNDING / SPONSORING ORGANIZATION: U. S. Army Research Office

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: DAAG29-84-K-0052

8c. ADDRESS *(City, State, and ZIP Code)*
P. O. Box 12211
Research Triangle Park, NC 27709-2211

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO

11. TITLE *(Include Security Classification)*: Molecular-Level Synthesis and Characterization of Metal-Polymer Interfaces

12. PERSONAL AUTHOR(S): Shaw Ling Hsu and Thomas J. McCarthy

13a. TYPE OF REPORT: FINAL

13b. TIME COVERED: FROM 4/16/84 TO 4/15/87

14. DATE OF REPORT *(Year, Month, Day)*: 1987, August 23

15. PAGE COUNT: 17

16. SUPPLEMENTARY NOTATION: The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*: metal, polymer, interface, surface, adsorption thin film, reflection-absorption spectroscopy

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

Two separate, but interacting research groups began a program entailing molecular level syntheses and characterization of metal-polymer interfaces. Two general synthetic routes were followed: In one case, a metal surface (platinum) was cleaned of its oxide layer by carrying out a hydrogenation reaction (hexene or cyclohexene) using the metal surface as the catalyst. Under these conditions, platinum oxide is unstable and is reduced to platinum(0) and water. The reaction was then deliberately poisoned with 4-picoline. Monitoring the kinetics of hydrogenation before and after the addition of the poison allowed us to determine that ~70% of the hydrogenation sites were ligated. The amount of 4-picoline that adsorbed was determined by elemental analysis, gravimetric analysis and UV-vis analysis of the

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT: ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION: Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL

22b. TELEPHONE *(Include Area Code)*

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

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solution. The surface-confined picoline was then deprotonated to render the ligated lithium reagent which was used to initiate the polymerization of styrene. The thin film of polystyrene prepared in this manner was irreversibly attached to the platinum surface. The platinum-polystyrene interface was studied by a range of analytical techniques. In the other case, a metal-polymer interface was prepared by polymer adsorption: Polystyrene containing one terminal thiol group and styrene-propylene sulfide block copolymers 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-labelled 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 thiol-terminated polystyrene. The effect of propylene sulfide block size on the number of adsorbed chains for a series of styrene-propylene sulfide block copolymers was determined. The technique of doubly modulated polarization Fourier transform reflectance infrared spectroscopy has developed as perhaps the most useful characterization method for thin films on metallic surfaces. Theoretical calculations were carried out to determine the theoretical limits of this technique and the technique has been perfected using thin films of discotic liquid crystals on gold surfaces. Well-resolved infrared spectra of thiol-terminated polystyrene monolayers on gold were obtained over the spectral range of 4000-500 cm^{-1}.

Molecular-Level Synthesis and Characterization of Metal-Polymer Interfaces

Introduction

Surface interactions between metals and polymers are central to a range of applications: corrosion inhibition, adhesive joint strength, electronics, modified electrodes, polymer-supported catalysis, decorative plating. In the last funding period (DAAG-29-84-K-0052) two separate, but strongly interacting research programs were started in Professors McCarthy and Hsu's laboratories. The first (McCarthy's) emphasized the preparation of thin films of polymers attached to metallic surfaces. The second program (Hsu's) concentrated on developing characterization techniques and characterizing polymer structure when adsorbed on metallic surfaces.

Two general synthetic approaches were taken: In one case polymers were attached to the metal surface by grafting from the surface. The metal was reduced and a ligand which was capable of being activated to an anionic polymerization initiator was attached. The initiator was activated and monomer was added. In the other case, polymer monolayers were formed by adsorption of polymers containing functionality with specific affinity for the metal. In both case irreversibly adsorbed polymer monolayers were prepared.

The materials were characterized by a range of techniques including contact angle analysis, gravimetric analysis, X-ray photoelectron spectroscopy and scintillation counting of radioisotope-labelled polymers. The major characterization emphasis was on vibrational spectroscopy, particularly infrared spectroscopy and the technique of doubly modulated polarization Fourier transform infrared spectroscopy was developed to be our most useful characterization tool.

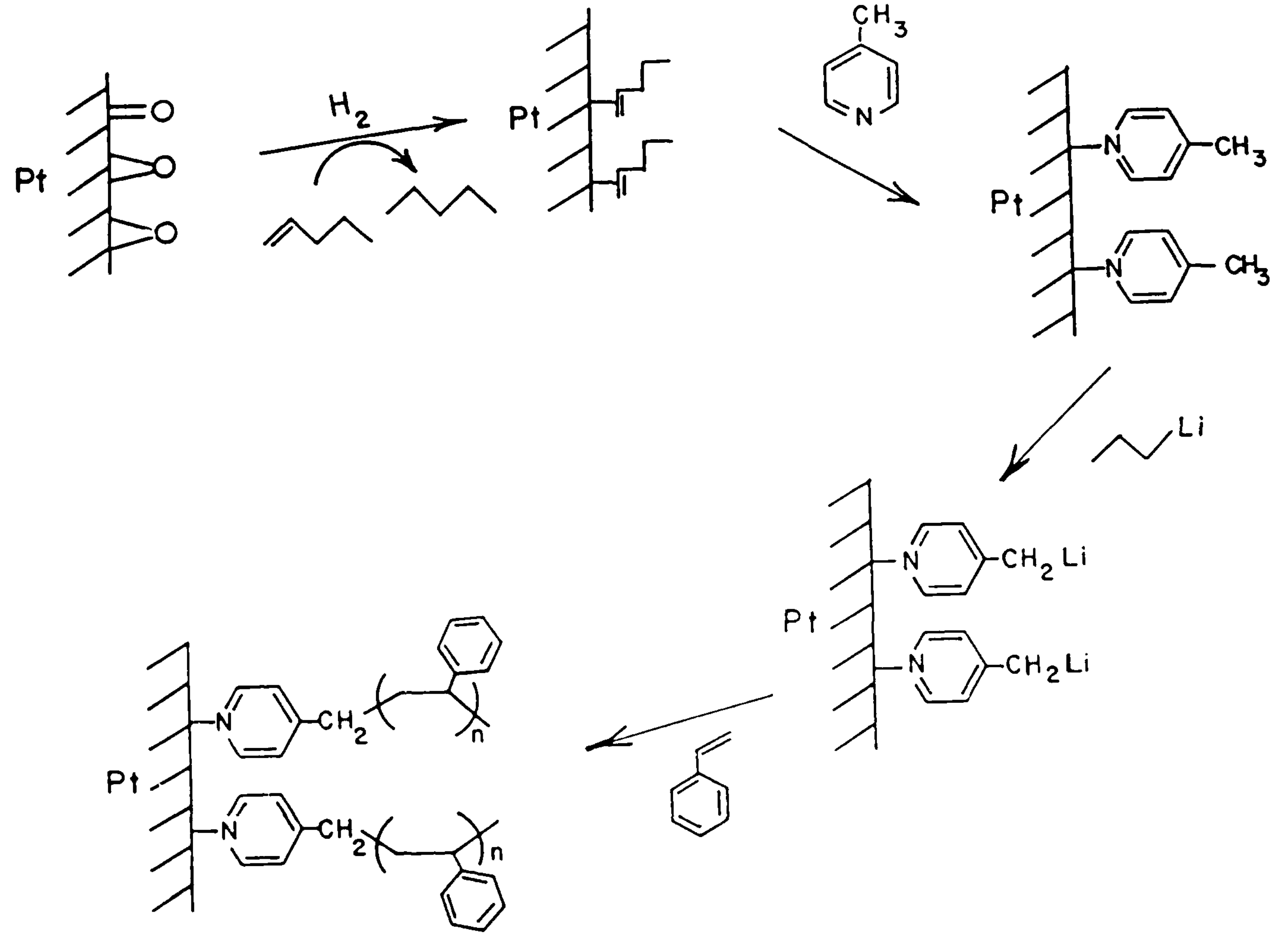
Progress

The work which we report here is more extensive than is indicated by this report. Specific references to publications are given and reprints and preprints are enclosed. Although we are not presently being funded by ARO, the work continues and more manuscripts in these areas are in different stages of preparation and will appear. This report includes only several examples of the materials we have prepared and the characterizations we have performed.

Synthesis

Platinum-Polystyrene[1]. One synthetic strategy for preparing a model metal-polymer interface was by grafting from the metal surface. In choosing the variables (metal, ligand, monomer, polymerization mechanism) for this approach, several requirements were considered: The metal had to be easily cleaned of its oxide coating under normal laboratory conditions (organic solutions) and available as a high surface area solid. We wanted to avoid high surface area supports to eliminate unnecessary complications. The ligand had to adsorb irreversibly or at least tenaciously and be capable of initiating polymerization. The monomer had to be suitable for analysis by a range of characterization techniques. We had a preference for anionic polymerization as it is the best technique for preparing monodisperse polymers. Additionally, these variables are not independent and had to be chosen collectively. **Scheme I** describes our choices and details our stepwise synthesis. Platinum is easily cleaned of its oxide coating by using it as a

Scheme 1



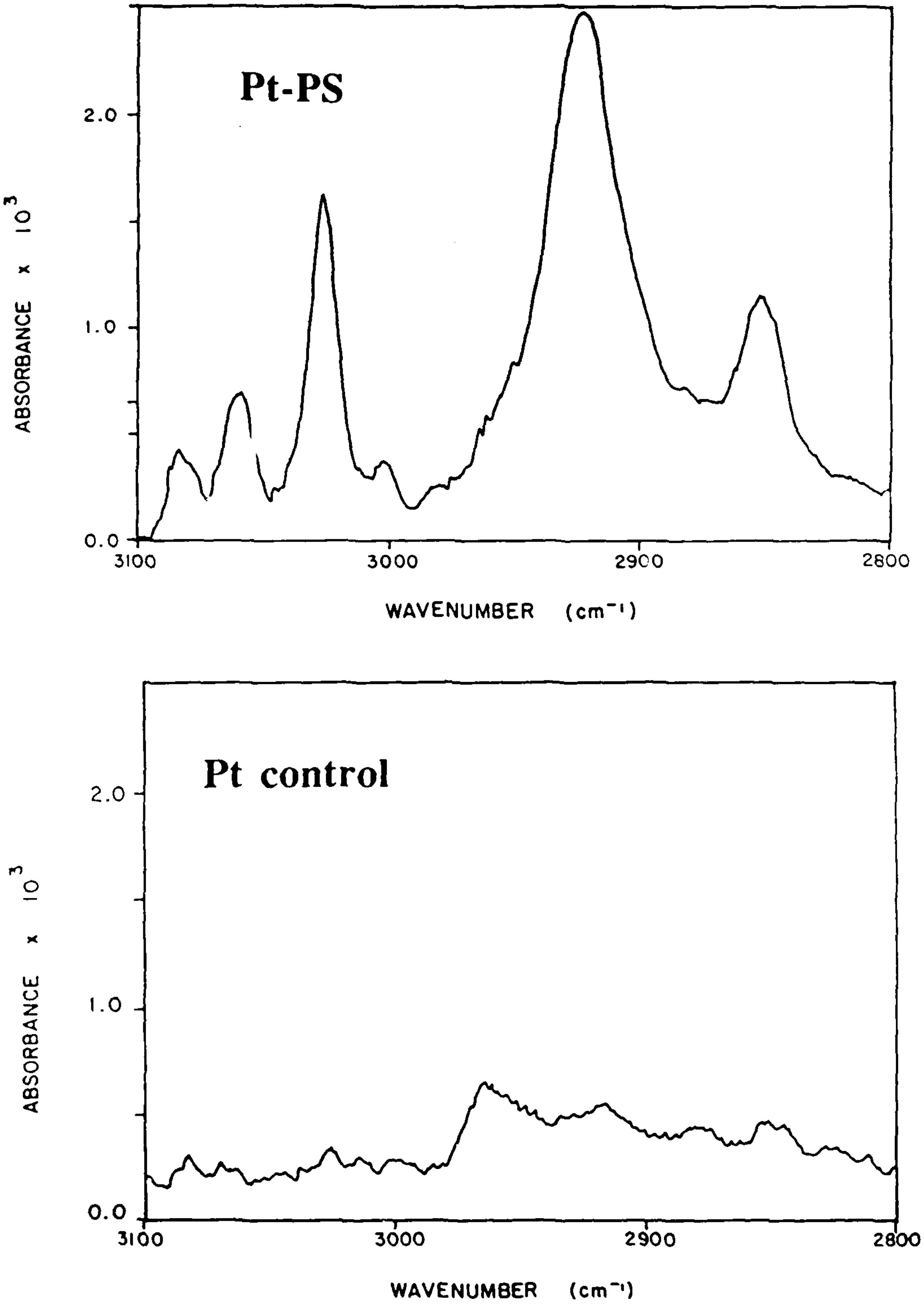
catalyst for an olefin hydrogenation reaction. It is available as a high surface area solid - platinum black. 4-Picoline was chosen as a ligand for two reasons: (1) It has been shown that pyridine adsorbs irreversibly[2] and perpendicular[3] to Pt(111). We assume that 4-picoline behaves analogously; this has been demonstrated for Ni(100).[4] (2) The pseudo-benzylic hydrogens of 4-picoline are acidic and can be removed to form an anionic polymerization initiator. Styrene can be anionically initiated to form monodisperse polymers which can easily be characterized by a range of techniques. **Table I** shows data of representative metal-polymer samples prepared as indicated in **Scheme I**. The molecular weight of the attached polymers was calculated from the elemental analysis (carbon and nitrogen) (Mn(obsd)). The values of Mn(calcd) were determined from the ratio of styrene to lithium reagent used. The numbers should be compared to realize that we have control over the molecular weight of the attached polymer, but cannot precisely prepare specific molecular weight samples. Infrared spectra of a platinum-polystyrene sample and a control (no 4-picoline added) are shown in **Figure 1**.

Table I

Calculated Molecular Weight

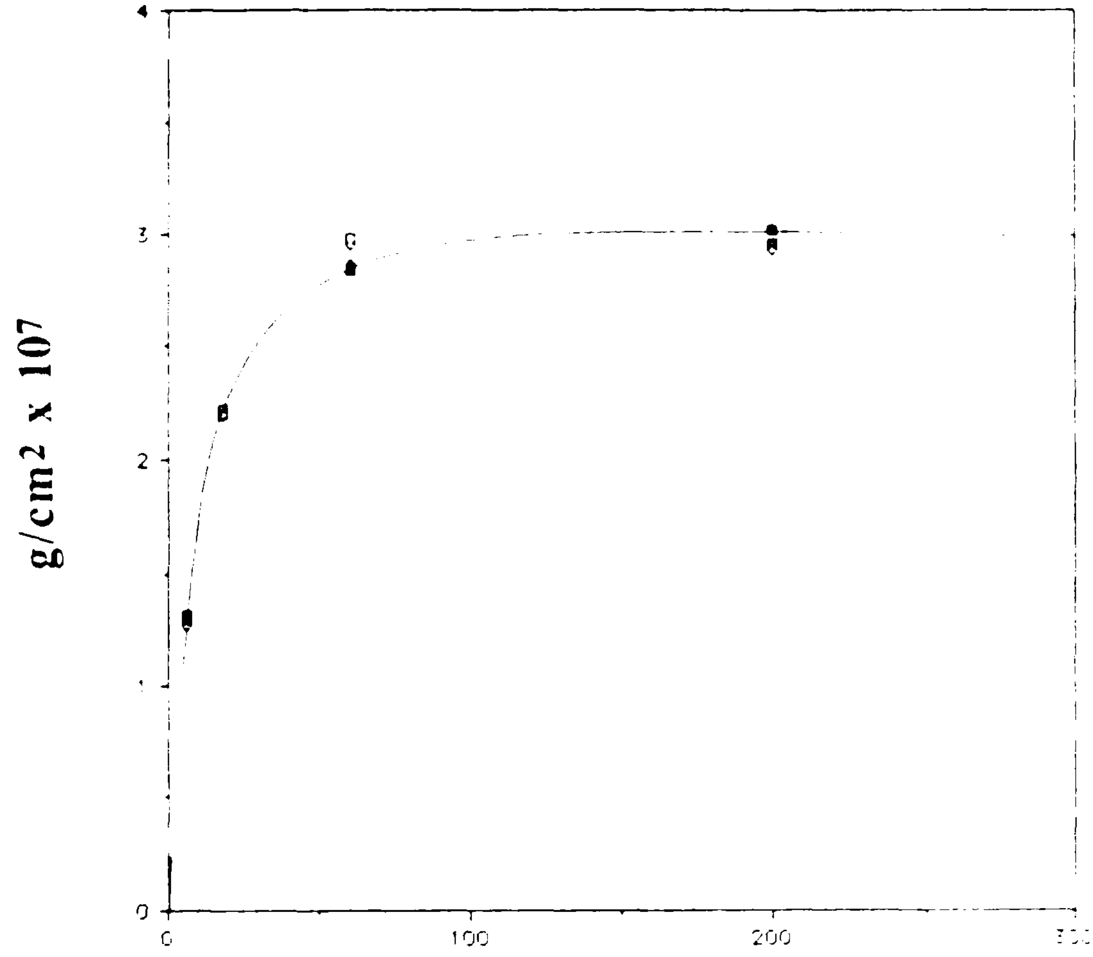
Sample	Mn (obsd)	Mn (calcd)
103a	1500	4023
131a	4040	8891
139a	660	1400
139b	570	1400

Figure 1


Pt-PS
2.0
1.0
0.0
ABSORBANCE x 10^3
3100
3000
2900
2800
WAVENUMBER (cm⁻¹)
Pt control
2.0
1.0
0.0
ABSORBANCE x 10^3
3100
3000
2900
2800
WAVENUMBER (cm⁻¹)

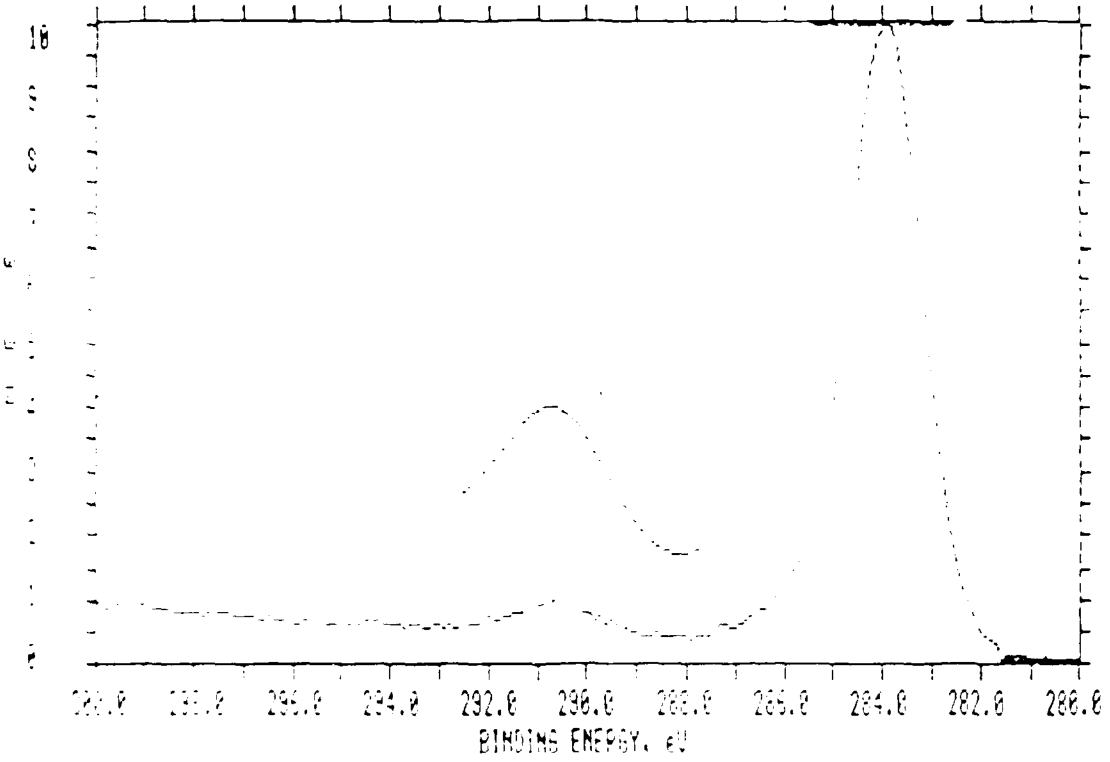
Gold-Polystyrene.[5] Polymer monolayers were prepared by the adsorption of thiol-terminated polystyrenes(PS-SH) and styrene-propylene sulfide block copolymers (PS-PPS) from solution onto glass-supported evaporated gold films. The adsorption was followed and the resulting monolayers were characterized by X-ray photoelecton 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 molecule is attached to the surface; no order in the polymer film is implied. Most of the experiments which we performed were adsorptions from THF, a solvent from which unmodified polystyrene does not adsorb.[6] PS-SH and PS-PPS are thus attached to the gold surface by gold-sulfur bonds. We have not carefully determined the kinetics of adsorption, but have determined conditions which reproducible, equilibrium polymer monolayers are formed. Adsorption experiments consisted of introducing polymer solutions (2 mg/mL in all experiments except the concentration studies - which varied from 0.02 to 3 mg/mL) to Schlenk tubes under nitrogen via cannula to cover the glass-supported films. Exposure times varied from several minutes to several days. In all cases, equilibrium adsorbance was reached after 1 h (there was no difference between 1 h and 24 h exposed samples by any analytical technique used). **Figure 2** shows adsorbance vs. molecular weight data as determined by LSC for PS-SH samples with molecular weights of 6000,18,000, 60,000 and 200,000. The highest molecular weight sample studied (500,000) did not adsorb. Evidently at a sufficiently high molecular weight (between 200,000 and 500,000), the interaction between the solvent and the polymer is great enough to inhibit sulfur-gold interaction and the thiol-terminated polystyrene behaves as though it were unmodified polystyrene. **Figure 3**

Figure 2



molecular weight x 10^{-3}

Figure 3


10
9
8
7
0
300.0
298.0
296.0
294.0
292.0
290.0
288.0
286.0
284.0
282.0
280.0
BINDING ENERGY, eV

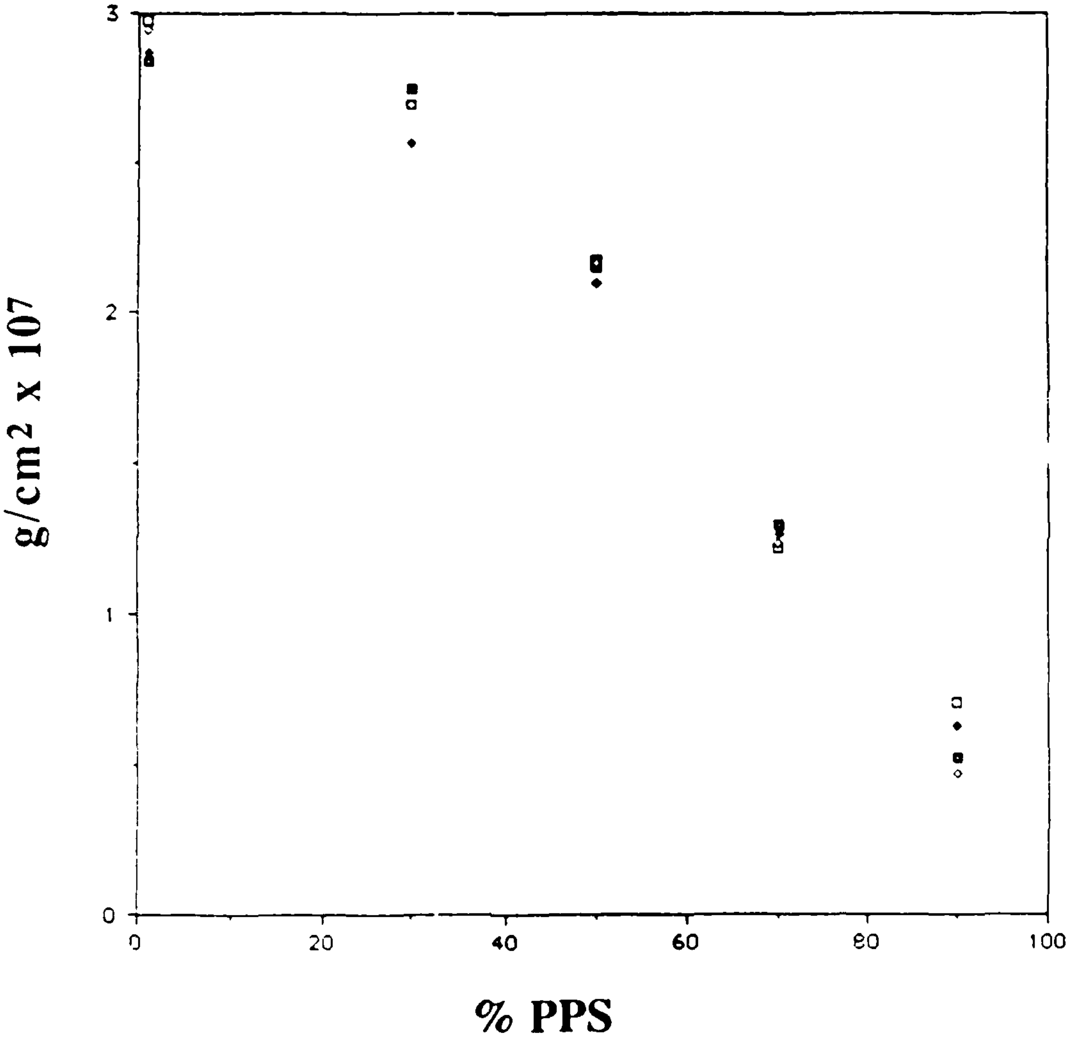
shows a C_{1s} XPS spectrum of a 135,000 molecular weight sample of PS-SH adsorbed to gold. That the carbon observed by XPS is due to polystyrene is verified by the π-π* shake-up satellite which is observed at 6.7 eV higher binding energy from the main C_{1s} photoelectron line.

A series of PS-PPS block copolymers were prepared with the propylene sulfide block varying from 1 to 90% molar content. **Figure 4** 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 glock, the fewer chains adsorb. This configuration was suggested[7] for styrene-vinylpyridine copolymers adsorbed on mica.

Infrared Characterization

External reflectance IR spectroscopy has been the principal characterization tool for this work. It has been useful in monitoring adsorption experiments and determining the number and type of functional groups at the surface. Potentially, infrared spectroscopy can determine the geometric orientation of ligands, the strength of the coordinative interaction, the effect of coordination on bond strength and bond geometry in the ligand, the yields of surface chemical transformations, the success of polymerization reactions, functional group gradients and other information. The utility of the specialized techniques of attenuated total reflectance, diffuse reflectance and external reflectance, especially when coupled to Fourier transform infrared spectrometers, has become apparent in the last few years, but sensitivity is still a problem. Most of the techniques are suitable for thick film studies (we should emphasize that the definitions of "thick and thin" have

Figure 4

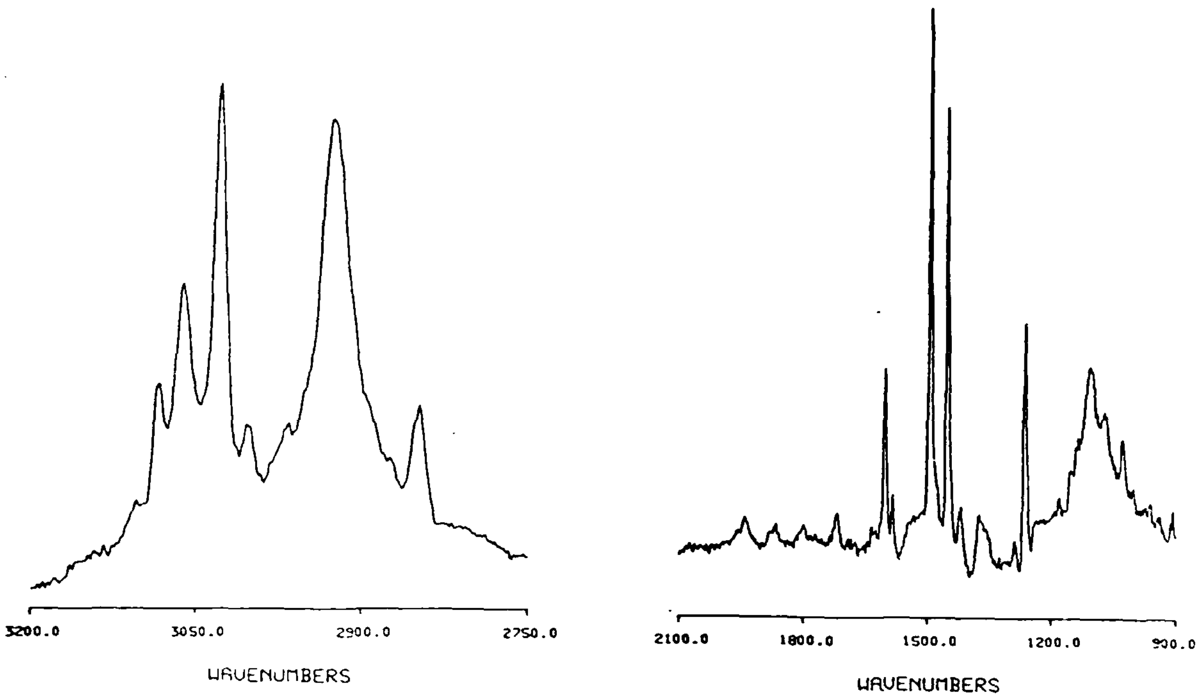


changed a great deal in the past few years), but have been generally unsuitable for monolayer and sub-monolayer regimes. For this purpose we have developed doubly modulated polarization Fourier transform reflectance infrared spectroscopy.

The principals behind the technique in fact are understood well. Basically, we take advantage of the difference in the absorption of two mutually perpendicular radiation beams reflecting from a metallic substrate covered with thin organic coatings. By modulating these two polarized beams, their differences can be enhanced with the use of a lock-in amplifier. Experimentally this technique is much more difficult than we had expected. It was not until earlier this year that our experiments reached the theoretical limits of this technique. **Figure 5** shows a spectrum of a PS-SH sample adsorbed to gold.

In addition to the work on polymer metal interfaces, considerable work has been done on adsorbed thin films of discotic liquid crystals. We do not discuss this here, but enclosed are reprints and preprints of this work.

Figure 5


3200.0
3050.0
2900.0
2750.0
WAVENUMBERS
2100.0
1800.0
1500.0
1200.0
900.0
WAVENUMBERS

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