

AN INTERDISCIPLINARY WORKSHOP

ON

**THE SCIENCE AND TECHNOLOGY OF POLYMER
INTERFACES**

sponsored by

**Division of Polymer Chemistry, Inc.
Division of Polymeric Materials:
Science and Engineering
American Chemical Society**

co-sponsored by

**Glass Division, American Ceramics Society Inc.
and the Metallurgical Society**

**The Hyannis Regency Inn
Hyannis, Massachusetts**

June 9-12, 1985

Sunday Evening, June 9, 1985

Registration and Welcoming Reception

7:00-10:00 P.M.

Monday Morning, June 10, 1985

SPECTROSCOPY AT POLYMER SURFACES AND INTERFACES

Chairman, E.J. Kramer

G.B. STREET 8:30 A.M.

"INTRODUCTION"

D.L. ALLARA, Bell Communications Research 8:35 A.M.

"SPECTROSCOPIC STUDIES OF POLYMER-METAL SURFACES"

J.J. PIREAUX, Facultes Universitaires 9:20 A.M.
Notre-Dame De La Paix

"ELECTRON SPECTROSCOPY OF POLYMER SURFACES"

B R E A K 10:05 A.M.

M. STAMM, Brookhaven National Labs 10:20 A.M.

"INVESTIGATION OF POLYMER INTERFACES BY NEUTRON SCATTERING"

A.W. CZANDERNA, Solar Energy Institute 11:00 A.M.

*"IR, SURFACE ANALYTICAL, AND SPECULARITY STUDIES OF
THE PMMA/AgCl/Ag AND PMMA/Ag INTERFACES"*

L.J. GERENSER, Kodak Research Labs 11:30 A.M.

*"APPLICATION OF ESCA AND CONTACT-ANGLE MEASUREMENTS
TO STUDIES OF AN ADSORBED FLUOROSURFACTANT"*

Monday Afternoon, June 10, 1985

POLYMER ADHESION

Chairman, D. Dwight

F.M. FOWKES, Lehigh University 2:00 P.M.

"ADHESION OF POLYMERS TO METALS AND CERAMICS"

J.P. BELL, University of Connecticut 2:45 P.M.

"THERMAL-SET BONDING TO COPPER AND STEEL"

B R E A K 3:30 P.M.

G. WHITESIDES, Harvard University 3:45 P.M.

*"ORGANIC SURFACE CHEMISTRY: OXIDIZED POLYETHYLENE
AND BONDED MONOLAYERS"*

Tuesday Morning, June 11, 1985

CHEMISTRY AND PHYSICS AT INTERFACES

Chairman, G. Whitesides

H.K. YASUDA, University of Missouri-Rolla 8:30 A.M.

"PLASMA POLYMERIZATION AT SURFACES"

J.T. KOBERSTEIN, Princeton University 9:15 A.M.

*"MEASUREMENT AND MODELLING OF POLYMER SURFACE AND
INTERFACIAL TENSION"*

B R E A K 10:00 A.M.

I. SANCHEZ, National Bureau of Standards 10:15 A.M.

"PHYSICS OF POLYMER-LIQUID INTERFACES"

J.F. ELMAN, Kodak Research Labs 11:00 A.M.

*"XPS, CONTACT ANGLE AND SER STUDIES OF PLASMA-TREATED
POLYETHYLENE"*

E.W. HELLMUTH, University of Missouri 11:30 A.M.

*"ELECTRODE SURFACE MODIFICATION BY GLOW DISCHARGE
POLYMER COATINGS"*

Tuesday Afternoon, June 11, 1985

CHEMISTRY AT INTERFACES

Chairman, T.C. Clarke

- P. HO, IBM Research Division 1:45 P.M.
"CHEMISTRY AND CHEMICAL REACTIVITY OF METAL POLYIMIDE INTERFACES"
- J.L. BREDAS, Facultes Universitaires 2:25 P.M.
"ELECTRONIC STRUCTURE CALCULATIONS ON POLYMERS. APPLICATION TO POLYMER SURFACES AND INTERFACES"
- B R E A K 3:05 P.M.
- T.J. McCARTHY, University of Massachusetts 3:20 P.M.
"CHEMISTRY AT CHEMICALLY RESISTANT POLYMER SURFACES"
- L.T. TAYLOR, Virginia Polytechnic Institute and State University 4:00 P.M.
"ELECTRICAL CHARACTERIZATION OF METAL CONTAINING POLYIMIDE FILMS"
- B.D. SILVERMAN, IBM T.J. Watson Research Center 4:20 P.M.
"MOLECULAR ORBITAL ANALYSES OF THE XPS AND UPS SPECTRA OF POLYIMIDE AND RELATED MODEL COMPOUNDS"
- J.W. BARTHA, IBM T.J. Watson Research Center 4:40 P.M.
"IMIDIZATION REACTION OF POLYAMIC ACID"
- P.N. SANDA, IBM T.J. Watson Research Center 5:00 P.M.
"XPS STUDIES OF THE POLYPHENYLENE OXIDE - COPPER INTERFACE"

Wednesday Morning, June 12, 1985

INTERACTIONS AT POLYMER SURFACES

Chairman, D.L. Allara

- D.W. DWIGHT, Virginia Polytechnic Institute 8:30 A.M.
"ION BEAM MODIFICATION OF POLYMER SURFACES"

E.J. KRAMER, Cornell University 9:15 A.M.

"PROBING POLYMER DIFFUSION AT POLYMER-POLYMER INTERFACES BY ION BEAM TECHNIQUES"

B R E A K 10:00 A.M.

J.F. RABOLT, IBM Research Division 10:15 A.M.

"SPECTROSCOPIC STUDIES OF ORDER-DISORDER TRANSITIONS IN THIN POLYMER FILMS AND LANGMUIR-BLODGETT MONOLAYERS"

M. TIRREL, University of Minnesota 11:00 A.M.

"FORCES BETWEEN POLYMER SURFACES"

INVESTIGATION OF POLYMER INTERFACES BY NEUTRON SCATTERING

M. Stamm⁺ and C. F. Majkrzak

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The method of neutron scattering has already extensively been applied to polymers in bulk and solution to reveal information about the molecular conformation and structure which is otherwise only difficult to obtain. Even if neutrons usually have a penetration depth of the order of some millimeters into polymeric materials, it is possible by some special techniques to obtain interesting information about polymer interfaces and surfaces. Two of these methods will be discussed: neutron small-angle scattering from polymer interfaces and total reflection of neutrons from polymer surfaces.

In the first technique, sandwich-like stacks of very thin films of alternating deuterated and non-deuterated material are heated above the melting or glass transition temperature to allow individual molecules a diffusional motion across the interface. This diffusion can be monitored by small-angle neutron scattering and information like the thickness of the interfacial layer, the diffusion coefficient and the chain conformation within the interfacial layer can be obtained.

With the second technique, for example, a thin polymer coating on a surface can be investigated. Neutrons are totally reflected from the surface and their reflection profile reveals information about thickness, density profile and conformation of the polymer layer. Some other applications of these techniques will be discussed.

**INFRARED SPECTROSCOPIC, SURFACE ANALYTICAL,
AND SPECULARITY STUDIES
OF THE PMMA/AgCl/Ag AND PMMA/Ag INTERFACES***

John D. Webb, J. R. Pitts, A. W. Czanderna,
Paul Schissel, H. H. Neidlinger, and T. M. Thomas

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Polymer/silver interfaces in solar energy systems will be exposed to solar ultraviolet and visible irradiation if the polymer is transparent. Specularity losses of pure PMMA/Ag/Glass multilayers may result from roughness of the polymer surface, roughness at the PMMA/Ag interface, or from reactions of the specimen during accelerated or real-time testing. Data are presented showing specularity losses for two of these three cases. For the third case, the rate of photodegradation of polymethylmethacrylate (PMMA) on clean silver, as measured using FTIR-RA spectroscopy is extremely slow under 10X terrestrial UV illumination (wavelengths longer than 285 nm). As shown in this work, however, the rate of photodegradation is accelerated substantially when the silver substrates are contaminated with chloride ions and results in visual darkening of the samples. IR-RA spectra of the contaminated samples taken before and after 1 h UV exposure reveal some accumulation of carbonyl at 1750 cm^{-1} and extensive loss of the PMMA carbonyl at 1731 cm^{-1} , as well as some loss of ester functionality from 1100 to 1300 cm^{-1} . There is also a general decrease in specularity of the samples. Other IR-RA spectra taken during the experiments reveal that most of the changes occur during the first fifteen minutes of UV exposure. Chlorine concentrations of up to 14 atomic per cent were determined using XPS on ion etched silver surfaces after the UV exposure. These observations are consistent with our hypothesis that the PMMA layer is photocatalytically altered by a silver chloride interfacial layer, with concurrent deposition of finely-divided silver at the interface.

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+A USDOE Laboratory.

Application of ESCA and Contact-Angle Measurements to Studies
of an Adsorbed Fluorosurfactant

L. J. Gerenser, J. M. Pochan, M. G. Mason, and J. F. Elman
Research Laboratories, Eastman Kodak Company, Rochester, New York
14650.

Abstract: ESCA and surface energy measurements were made on clean SiO_2 and poly(ethylene terephthalate) (PET) films coated with various amounts of the cationic fluorosurfactant Zonyl FSC. On SiO_2 , ESCA measurements show that the fluorosurfactant coverage is uniform and continuous at all coating thicknesses and the surfactant molecules reorient within certain coating regimes. Good agreement was found between calculated surfactant coverages, based on proposed molecular orientations, and actual values determined from ESCA measurements in a region where only a monolayer of surfactant is coated. On PET, ESCA measurements indicate incomplete surface coverage with possible aggregation even at coverages where the average thickness is considerably greater than that of a monolayer. Models and correlations are derived to relate dispersion energy measurements to measured ESCA surface coverage.

Adhesion of Polymers to Metals and Ceramics

F. M. Fowkes

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Lehigh University
Bethlehem, PA 18015

The adhesion of polymers to substrates such as the metal oxide surface of metals or the surface of ceramics (including oxides, nitrides, carbides, etc.) can be very appreciably enhanced by the interaction of acidic or basic sites of the polymer with basic or acidic sites of the substrate. These interactions, formerly called "polar" interactions, are completely independent of dipoles, but can be quantitatively predicted by the surface concentrations and the Drago E and C constants of the interacting sites. Calorimetric and spectroscopic techniques for determining E and C constants for polymers and for inorganic surfaces have been developed. Coupling agents are found to function by conferring acid or basic surface sites.

Examples of enhanced adhesion achieved by controlled acid-base interfacial interaction will be reviewed.

Measurement and Modelling of Polymer

Surface and Interfacial Tension

Jeffrey T. Koberstein
Polymer Materials Program
Department of Chemical Engineering
Princeton University
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The structure and properties of polymeric surfaces and interfaces are important to the technologies of many industrial processes. Surface tension and wetting, for example, are important to the manufacture of thin films and coatings. The behavior of polymer-polymer interfaces affects greatly the adhesion in multilayer composites, the particle size and stability of polymer blend dispersions, and the general mechanical integrity of multiphase polymers. The single most accessible experimental parameter that characterizes polymer interphases is the surface or interfacial tension. The general dependence of the tension on parameters such as molecular weight and temperature are illustrated using a number of literature examples. The determination of these tensions may be accomplished by analysis of fluid-drop profiles by means of digital image-processing of these profiles with the aid of robust shape-comparison algorithms. This method is applied to measure the surface tension of poly(dimethyl siloxane) and the interfacial tension of immiscible blends of poly(dimethyl siloxane) with polybutadiene as a function of temperature and molecular weight. These results are compared to the predictions of current theories of polymer interphase properties. In the case of interfacial tension the experimental data are used to extract the temperature dependence of the apparent interaction parameter.

XPS, Contact Angle, and SERS Studies of
Plasma-Treated Polyethylene

L. J. Gerenser, J. F. Elman, D. A. Glocker, and J. L. Lippert

Chemically specific gas-phase reactions have been used to tag plasma-induced chemical species on the surface of polyethylene. These tag reactions provide distinct moieties that can be detected via XPS to provide a surface count of induced species. Hydroxyl, epoxy, hydroperoxy, carboxylic acid and carbonyl populations are discussed as a function of plasma atmosphere, time after treatment and water washings. Preliminary adhesion and Surface Enhanced Raman (SERS) results will also be discussed.

ELECTRODE SURFACE MODIFICATION BY GLOW DISCHARGE POLYMER COATINGS.

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University of Missouri-Kansas City
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ABSTRACT

Electrical and electrochemical properties of plasma polymerized propylene on platinum were determined in mercury, aqueous and non-aqueous systems. The glow discharge polymerized propylene forms, under specific conditions, coatings which adhere well on metals and glass. Electrodes (coated platinum wires or micro disk electrodes, Pt diameter 150 μ m) were used in polarographic reduction of oxygen and analytical determination of metals. The coating was also applied on glass-electrodes. In polarographic studies it could be shown that poisoning, effects of stirring and pH variations can be reduced and minimized. Properties of the coatings depend on thermal annealing, i.e. the detection limit in stripping voltammetry were greatly improved.

CHEMICAL BONDING AND REACTION AT METAL-POLYMER INTERFACES

Paul S. Ho

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ABSTRACT

Knowledge on the properties of the metal-polymer interface is of basic interest for the development of microelectronic devices. A combination of surface spectroscopy and microanalytical techniques have been used to investigate the chemical and material characteristics of interfaces formed between metal and a high temperature polymer, polyimide. Results reveal significant chemical reactivity at the interface, as manifested by intermixing and cluster formation. The extent of the material reaction is strongly influenced by the bonding characteristics between metal and the polyimide. Results on several metals are reviewed to illustrate the chemical trend due to increasing reactivity.

CHEMISTRY AT CHEMICALLY RESISTANT
POLYMER SURFACES

Thomas J. McCarthy

Polymer Science and Engineering Department
University of Massachusetts
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The extent to which the body of knowledge commonly referred to as "organic chemistry" can be applied to functional groups on solid surfaces is not obvious. Geometry and surface physics are expected to play a more important role in determining the outcome of reactions when chemistry is confined to two dimensions. The talk will emphasize synthetic approaches to two-dimensional arrays of functional groups on chemically resistant polymers and the analytical chemistry involved in studying these reactions.

ABSTRACT

ELECTRICAL CHARACTERIZATION OF METAL CONTAINING POLYIMIDE FILMS

J. D. Rancourt, R. K. Boggess and L. T. Taylor
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Interesting thin film materials have been prepared by doping polyimides with metal salts and organometallic compounds. A variety of additives have been studied which represent the elements Li, Al, Co, Cu, Sn, Ag and Au. Thermal imidization of the prepolymer promotes chemical modification of the additive and in-part phase separation to the polymer surface in the resulting material. Two patterns of reactivity have generally been observed in a forced air atmosphere: conversion to the metallic state (noble metals) or conversion to a metal oxide (representative metals). Because a principal goal of the laboratory work was to produce materials having substantially modified electrical properties, the direct current electrical resistivity of the polyimide films has been measured at both room temperature and elevated temperature in vacuum. Data pertaining to the enhanced conductivity of the metal-oxide surfaces will be presented. Also, the bulk and surface d.c. electrical properties of the tin modified, cobalt modified, and non modified films will be compared.

**Molecular Orbital Analyses of the XPS and UPS
Spectra of Polyimide and Related Model Compounds**

**B. D. Silverman, P. N. Sanda, P. S. Ho
J. W. Bartha, and A. R. Rossi**

Abstract

Photoelectron spectroscopy (XPS, UPS) has been an effective tool in characterizing the surface of technologically important polymers such as polyimide. The present paper will discuss the role played by molecular orbital calculations in contributing to our understanding of the origin of the XPS and UPS spectra of polyimide and related model compounds. Topics discussed will include the origin of the C1s level splittings and the effect of water as well as bound metals on the spectra.

Imidization reaction of polyamic acid

J.W. Bartha, J.G. Clabes, B.D. Silverman, P.S. Ho

IBM T.J. Watson Research Center,
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and

A.R. Rossi

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Abstract:

The preparation of an intrinsic polyimide surface is required for photoemission spectroscopic studies of polyimide surfaces or interfaces. It has been found that a reproducible method is to cure the polyamic acid by annealing it in an ultra high vacuum. We have used UPS and XPS techniques to investigate the chemical nature of this phenomenon for polyimide before and after imidization. In addition molecular orbital calculations for the core levels as well as for the valence band structure have been used to derive a fundamental understanding of the experimental results.

XPS Studies of the Polyphenylene Oxide - Copper Interface

P. N. Sanda, J. G. Clabes, P. S. Ho, B. D. Silverman
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Abstract

We will discuss XPS studies of the interaction of polyphenylene oxide (PPO) with Cu. PPO consists of phenyl rings connected by oxygen atoms in ether linkages, and is therefore an ideal model polymer to aid in understanding the properties of the "ODA" constituent of PMDA - ODA polyimide. The samples were made from a solution of PPO in toluene and spin coated onto a Si wafer resulting in a thin continuous film. Spectra were recorded before and after sequential in-situ Cu depositions at different temperatures. The C1s and O1s spectra show changes upon deposition of Cu. The interaction of Cu with the ether group appears in two ways. First, a loss of intensity is observed for the peak corresponding to the C1s core level that originates from the carbon atoms in the ether linkages. Second, a new O1s peak appears at lower binding energy, suggesting a charge transfer to the oxygen. We also observe a decrease of the $\pi \rightarrow \pi'$ shake up structure which suggests that the π orbitals are involved in bonding with Cu. Deposition at elevated temperature (200 degrees Centigrade) indicates diffusion of Cu without a qualitative change in the Cu interaction with PPO.

Spectroscopic Studies of Order-Disorder Transitions in Thin
Polymer Films and Langmuir-Blodgett Monolayers

J. F. Rabolt
IBM Research Laboratory

Spectroscopic methods (UV-Vis, FTIR, Raman) have been used in conjunction with x-ray diffraction measurements to investigate order-disorder transitions in a series of poly(di n-alkylsilanes). Results suggest that the nature of the high temperature phase transition which gives rise to dramatic changes in the electronic structure originates from conformational disordering of the backbone due to a rapid melting of the n-alkyl side chains. Similar studies on Langmuir-Blodgett monolayers of long chain fatty acid salts at elevated temperatures reveals a much more gradual disordering mechanism which extends over a 90 C range culminating in an irreversible destruction of the head group "lattice". Spectroscopic measurements on polymer monolayers suggests that covalent bonding of the head groups significantly enhances the thermal stability of Langmuir-Blodgett films.

Direct Measurement of Forces between Polymer Layers

Matthew Tirrell

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Forces that develop between layers of polymers brought into intimate contact are the crux of many technologically important situations including adhesion, welding, polymer blends, microelectronics, stabilization and flocculation of colloidal suspensions. The resultant force depends upon: van der Waals' forces between the segments, the chemical environment, the nature of any substrate on which the layers are coated, molecular weight and degree of interpenetration. We have been studying these forces with an apparatus capable of measuring directly force vs. distance profiles between polymer surfaces in the separation range 0 to 2000 Å. This device is similar to that developed by Israelachvili and coworkers.

Thus far, our attention has been directed principally to adsorbed polymer layers immersed in solvent. In particular, we have been studying styrenic polymers and block copolymers as a function of molecular weight and solvent quality. Our accomplishments to date include a quantitative determination of the strength of bridging forces, a demonstration that polymers move and rearrange on the surface in response to applied forces and the first measurements of repulsive forces with block copolymers.

References:

1. "Forces Between Two Layers of Adsorbed Polystyrene Immersed in Cyclohexane Below and Above the Theta Temperature," M. Tirrell, J.N. Israelachvili, J. Klein and Y. Almog, *Macromolecules*, 17 204-209 (1984).
2. "A Theory for the Molecular Weight Dependence of Healing and Brittle Fracture in Amorphous Polymers Above the Critical Entanglement Molecular Weight," M. Tirrell, D.B. Adolf and S. Prager, *J. Polymer Sci., Polymer Phys. Ed.*, 23, 413-427 (1985).
3. "Forces Between Mica Surfaces Bearing Mobile, Adsorbed Polymer", M. Tirrell, S. Granick and S. Patel, *Macromolecules*, submitted (1985).
4. "Forces Between Block Copolymer Layers Adsorbed on Mica", M. Tirrell, S. Patel, G. Hadziioannou and S. Granick, *J. Colloid Int. Sci.*, submitted (1985).

PROBING POLYMER DIFFUSION AT POLYMER-POLYMER INTERFACES
BY ION BEAM TECHNIQUES

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and the Materials Science Center
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Rutherford backscattering spectrometry (RBS) and forward recoil spectrometry (FRES) are two new techniques being developed at Cornell for investigating diffusion in polymers. Both detect the numbers and energies of nuclei emerging from a polymer film which is bombarded with a high energy (2-3MeV) beam of He^{++} ions. In the case of RBS the He^{++} ions elastically scattered back from heavier nuclei in the film are detected whereas in the case of FRES hydrogen and deuterium nuclei recoiling in the forward direction are detected. Since energy and momentum are conserved in the nuclear collisions at these energies and since the probabilities of collisions with various nuclei (scattering crosssections) are well known, the number vs energy plot (RBS or FRES spectrum) from a thin film (<10nm) gives directly the chemical (nuclear) composition of the film. However since the He, H or D nuclei lose energy through collisions with electrons while travelling into or out of thicker films, a collision with a nucleus significantly below the surface results in shift in the spectrum to lower energies. By analysing the spectra from such samples in detail, concentration vs depth profiles of various nuclear species can be determined with a depth resolution of 10 to 100nm and a concentration sensitivity of better than 1 percent. This talk will present recent examples of the use of these techniques to investigate the movement of slowly diffusing polymer molecules near interfaces between polymer films.

Electron spectroscopy of polymer surfaces

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Auger Electron Spectroscopy (AES), X ray induced Photoelectron Spectroscopy (XPS), Ultraviolet Photoelectron Spectroscopy (UPS), and Electron Energy Loss Spectroscopy (ELS and HREELS) are five techniques using electrons to study material surfaces. Among them, AES and ELS are seldom used to characterize polymer surfaces, because of radiation damages induced by the probing electron beam.

XPS or ESCA on the contrary has been widely used to elucidate the chemical composition of polymer surfaces. For this purpose, almost exclusively core level analyses were performed, because of the ease of the method and the richness of the results that might be gained; as many contributors to this workshop will present examples of this type of ESCA applications, our presentation will focus onto the informations that can be gained from XPS valence band spectra of polymers. It will be shown that, with the use of complementary informations from UPS and quantum mechanical calculations (density of states), very valuable studies can be performed; examples will be chosen between substitution effects, isomerism, structural and conformational analysis of the polymeric chains.

Actually, HREELS (High Resolution Electron Energy Loss Spectroscopy) shows great promise to get another insight on the real extreme surface of polymers. The very first *electron induced vibrational spectra* of polyethylene will be presented and compared to Ir-Raman data: the vibrational bands will be assigned, and their intensities studied in the light of the dipolar interaction mechanism. It will be proven that this technique is very surface sensitive and that the polymer surface is to be considered as a "condensed gas", instead of a real solid state material.