

# An ACS Sponsored Interdisciplinary Workshop on Polymer Surfaces and Interfaces

October 20-23, 1996

at

The Tradewinds, St. Petersburg, FL.

**Sunday, 20 October, 1996**

4:00 PM **REGISTRATION**

5:30PM **WELCOMING RECEPTION** "Cash Bar"

**Thin Film Display Devices**

Chair: S. Kumar

7:00PM T.P. Russell, University of Massachusetts, Amherst: Rubbed Polymer Surfaces.

8:00 PM J.S. Patel, Pennsylvania State University, University Park, PA: The Role of Polymer Surfaces in Complex Liquid Crystal Devices.

**Monday, 21 October, 1996**

7:30 AM **BREAKFAST**

**Layered Systems: Devices**

Chair: A. Mayes

8:15AM G. Hadziioannou, University of Groningen, The Netherlands: Role of Interfaces and Phase Separation on Polymer LEDs, Photodiodes and Solar Cells.

9:15AM M.F. Rubner, Massachusetts Institute of Technology, Cambridge, MA: Layer by Layer Assembly of Polyions: New Opportunities for the Fabrication of Thin Film Devices.

10:15AM **Break**

**Layered Systems: Composites**

10:30AM G.S. Ferguson, Lehigh University, Bethlehem, PA: Mosaic Tiling in Molecular Dimensions: A Stepwise Chemical Approach to Nanostructural Composite Films.

11:30AM E.P. Giannelis, Cornell University, Ithaca, NY: Polymer-Layered Silicate Nanocomposites: Opportunities and Critical Issues.

12:30PM **Lunch** "On your own"

**Thin Films Dynamics**

Chair: A. Yethiraj

3:00 PM W.-L. Wu, NIST, Gaithersburg, MD: Glass Transitions of Thin Polymer Films.

4:00 PM S.H. Anastasiadis, FORTH, Greece: Dynamic Light Scattering from Polymer Brushes.

5:00PM **POSTER SESSION**

DINNER "On your own"

Tuesday, 22 October, 1996 Chair: A. Karim

7:30AM BREAKFAST

**Fundamentals of Wetting**

9:00 AM J. Klein Weizmann Institute of Science, Rehovot, Israel: Surface Enrichment and Wetting in Model Polymer Mixtures.

10:00 AM L. Leibler C.N.R.S., France: How do Polymer Layers Alter the Dynamics of Wetting ?

11:00AM Break

11:15AM D.Y. Yoon, IBM Almaden Research Center, San Jose, CA: Wetting and Mobility Characteristics of Thin Liquid Films of Perfluoroalkylether Lubricants on Solid Surfaces.

12:15PM Lunch "On your own"

**Adhesion and Composites** Chair: S. Anastasiadis

2:00 PM E.J. Kramer, Cornell University, Ithaca, NY: Kinetics of Grafting Chains at Polymer Phase Boundaries: Implications for Compatibilization of Immiscible Polymer Alloys.

3:00PM A.C. Balazs, University of Pittsburgh, Pittsburgh, PA: Modeling the Behavior of Polymers at Impenetrable and Penetrable Interfaces.

4:00 PM Break

4:15 PM L.T. Drzal, Michigan State University, E. Lansing, MI: Structure-Property Relationships for Polymer Interphases in Fiber Reinforced Composite Materials.

7:00PM BANQUET

Wednesday, 23 October, 1996

7:30AM Breakfast

**Biopolymers**

Chair: A. Mayes

9:00 AM B. Ratner, University of Washington, Seattle, WA: Control of Proteins at Interfaces.

10:00 AM L.G. Cima, Massachusetts Institute of Technology, Cambridge, MA: Tethered Ligands for Controlling Cell Behavior.

## **Surface Alignment of Polymers**

**T. P. Russell**

Polymer Science Department  
University of Massachusetts  
Amherst, MA

### **Abstract**

A poorly understood, yet, important step in the production of flat panel displays is the buffing of a polyimide film with a velour cloth. In contact with such a surface, liquid crystals form a monodomain with the molecules aligned in the direction of buffing. The literature is replete with explanations ranging from surface corrugations to oriented electrostatic surface fields on the polyimide. Results from grazing incidence x-ray scattering and near edge x-ray absorption fine structure studies have shown quantitatively that the polyimide chains only near the surface are aligned during buffing. This alignment is quite high which, given that the polymer is well below its glass transition temperature, is quite remarkable.

# **The Role of Polymer Surfaces in Complex Liquid Crystal Devices**

**J. S. Patel**

Department of Physics  
Department of Electrical Engineering and IMRL  
The Pennsylvania State University  
University Park, PA 16802

## **Abstract**

We will discuss the role of polymer surfaces in liquid crystal alignment. We will show how complex orientation of the liquid crystals is possible using conventional rubbing techniques. Using such surfaces we will discuss novel device structures based on liquid crystals but which are polarization independent. Specifically, the polarization independent operation Fresnel lens will be detailed.

**Role of Interfaces and Phase Separation on Polymer LEDs,  
Photodiodes, and Solar Cells**

**G. Hadziioannou**  
University of Groningen  
The Netherlands

## **Layer-by-Layer Assembly of Polyions: New Opportunities for the Fabrication of Thin Film Devices**

**M. F. Rubner**

Department of Materials Science and Engineering, MIT  
Cambridge, MA 02139

### **Abstract**

For many years, it has been known that ultra-thin, molecular-scale layers of charged polymers will spontaneously adsorb onto surfaces from dilute aqueous solutions. Recently, it has been found that this very simple adsorption process can be utilized to fabricate multilayer assemblies of polyions in a layer-by-layer processing mode. In this process, molecular layers of oppositely charged polymers are alternately deposited onto a substrate to create multilayer thin films in which the layer sequence and thickness can be controlled at the molecular level. With such multilayers, it is possible to readily modify the wettability of surfaces as well as to create heterostructure thin film devices of electronically active polymers. For example, we have fabricated large area, thin film light emitting devices based on multilayer heterostructures of poly (p-phenylene vinylene) (PPV) and various polyanions. The nature of the polyanion used to assemble the PPV multilayers was found to dramatically influence the emission wavelength, intensity and charge transport capabilities of the thin films. Active layer thicknesses as thin as 80 Å were readily prepared using this new technique. Light emitting devices with high luminance levels ( $>500$  cd/m<sup>2</sup> in the range of 5-12 volts) and tunable emission wavelengths have been created through the use of multi-bilayer "slab" systems that are used to control the charge injection and transport characteristics of the device. Since this is a molecular layer-by-layer fabrication technique, it is also possible to readily manipulate the nature of the polymer/electrode interfaces present in these devices. Details concerning the behavior of these new devices and the mechanisms of charge injection and transport operating in these new multilayer thin films will be discussed.

**Mosaic Tiling in Molecular Dimensions: A Stepwise, Chemical Approach  
to Nanostructural Composite Films**

**Gregory S. Ferguson**  
Department of Chemistry  
Lehigh University  
Bethlehem, PA 18015-3172

**Abstract**

The assembly of molecules as intact constituents to form larger, more complex structures has led to recent advances in the preparation of thin films and extended solids. We have developed a chemical approach for the stepwise preparation of ordered multilayers by sequential adsorption of two components- a cationic polymer and an anionic sheet-silicate mineral - from aqueous solution or suspension onto various surfaces. These films are sufficiently ordered in the direction normal to the substrate surface to diffract x-rays, and have lattice spacings of nanometer dimension. This talk will focus on the synthesis of these multilayers, analysis of their composition and structure, and studies of their properties. Particular attention will be given to new design principles developed in the course of these studies.

## **Polymer-Layered Silicate Nanocomposites: Opportunities and Critical Issues**

**Emmanuel P. Giannelis**  
department of Materials Science & Engineering  
Cornell University  
Ithaca, NY

### **Abstract**

Composites with dimensions in the range of 1 nm to 100 nm, so-called nanocomposites, are the subject of intense current research and development. At Cornell we have focused on the design and synthesis of polymer-ceramic nanocomposites using intercalation of layered ceramics. This approach exploits the ability of layered ceramics to intercalate a wide variety of organic and inorganic chemicals in the galleries formed between the ceramic layers having thicknesses on the nanometer scale. In general, nanocomposites formed by intercalation of layered ceramics are found by us and investigators around the world to possess properties not limited by the rules of mixtures, but, rather, exhibit a synergism of the components. Specifically, they exhibit a combination of strength and thermal and dimensional stability which cannot be attained by a simple mixture of the components. In this talk I will review the strategies to synthesize various thermoplastic, thermosetting and elastomeric nanocomposites, present their properties, and discuss their potential applications. Specific issues related to the thermodynamics and kinetics of polymer intercalation and its effect on rheology will be emphasized.



## Ultra-Thin Polymer Film Properties on Silicon

W. Wu, Eric K. Lin, W. E. Wallace,  
Polymers Division  
NIST,  
Gaithersburg, MD

J. H. van Zanten  
Department of Chemical Engineering  
Johns Hopkins University  
Baltimore, MD

### Abstract

The coefficient of thermal expansion, CTE, and the glass transition temperature,  $T_g$ , of polymer thin films were determined to examine their dependence on the interaction energy with the substrate. To approach the interface behavior, the film thickness included in this work was as low as 50Å. X-ray and neutron reflectivity were used to determine film thickness.  $T_g$  and CTE were determined by monitoring the film thickness as a function of temperature. Some preliminary results of buried thin films will also be discussed.

Polystyrene (PS), poly (methyl methacrylate) (PMMA) and poly 2-vinyl pyridine (P2VP) were included in this study. Among these polymers their interaction energy with silicon can be ranked as P2VP > PMMA > PS. The results indicated that film properties depended strongly on the polymer/silicon interaction.

# Evanescent Wave Dynamic Light Scattering from Adsorbed Diblock Copolymers at Solid Surfaces\*

S. H. Anastasiadis<sup>†</sup>

Foundation for Research and Technology-Hellas,  
Institute of Electronic Structure and Laser,  
P. O. Box 1527, 71110 Heraklion, Crete, GREECE

## Abstract

Polymer chains attached by one end to an impenetrable surface at high coverage exemplify a tethered layer of mesoscopic dimensions. At equilibrium, thermal fluctuations of the segment density profile of the brushlike layer reflect the tethered chain dynamics; the probing of these fluctuations by dynamic light scattering in the evanescent wave configuration is reported. In this setup, the evanescent light illumination, produced under the wavevector  $q$  using photon correlation spectroscopy and taking advantage of its broad time range ( $10^{-7}$ - $10^{-3}$ s). A set of terminally-attached layers with thicknesses ( $L_0$ ) from 45 to 130 nanometers is utilized, and the experiments demonstrate the applicability of the evanescent wave dynamic light scattering to study dynamics of tethered chains. It is found that there is a preferred wavelength of  $O(L_0)$  of these fluctuations with a concurrent slowing down of their thermal decay rate, similarly to the internal relaxation in bulk diblock copolymer solutions. This technique could open the route for the investigation of the largely unexplored area of polymer surface dynamics.

---

\*Part of this research was sponsored by the European Union (Israel/EC Joint Research Project: CI1\*-CT93-0351) and by NATO's Scientific Affairs Division in the framework of the Science for Stability Programme

<sup>†</sup> In collaboration with G. Fytas, D. Vlassopoulos, C. Toprakcioglu, J. Li, B. Factor, R. Seghrouchni, W. Theobald, A. N. Semenov, A. Likhtman

## Surface Enrichment and Wetting in Model Polymer Mixtures

**Jacob Klein**  
Weizmann Institute of Science  
Rehovot, Israel

### Abstract

Random copolymers of composition  $A_xB_{1-x}$  may be viewed as molecules whose mean properties can be 'tuned' continuously from pure A ( $x = 1$ ) to pure B ( $x = 0$ ), and as such serve as excellent model mixtures for examining wetting and surface enrichment behaviour. We have carried out a comprehensive study of such mixtures, where A and B are olefines with varying branching ratios, and thus different flexibilities, along isotherms in the phase coexistence space, right up to the binodal line. Our results suggest that entropic effects play an insignificant role in determining the surface enriched species in such mixtures. A Cahn-type analysis sheds new light on the nature of the wetting transition in these model binary blends.

## How Do Polymer Layers Alter the Dynamics of Wetting?

Ludwik Leibler

Systems Macromoleculaire Heterogenes, U. M. R. C. N. R. S. - ELF Atochem  
C. A. L., 95 rue Danton, B. P. 108, 92303 LEVALLOISE Perret CEDEX France

### Abstract

In many useful systems such as paints, adhesives, and textiles, solid surfaces are protected by soft absorbed polymer layers. Protective films enable one to control the wetting properties of the surfaces as their presence modifies the solid surface tension. The aim of the present talk is to discuss how the kinetics of spreading of liquids on polymer protected surfaces can be profoundly modified by dissipative processes that occur in surface layers. We consider in particular surfaces covered by terminally anchored polymer chains (so called polymer brushes). We propose a model which describes both statics and dynamics of partial wetting of nonsoluble liquids on such films. We predict that the presence of a molten polymer layer can spectacularly slow down the spreading process. For lightly cross-link rubbers we show that the dissipated power varies as  $V^{1+m}$  (where  $V$  is the spreading velocity and the exponent  $m$  is not universal, but depends on the presence of dangling chains and on the temperature). Hence, the dynamics of spreading can be controlled by an appropriate choice of polymer chemical structure or by incorporation of a plasticizer in a polymer layer. Indeed, by changing the temperature in the glass transition region, the spreading velocity can be tuned and varied by many orders of magnitude. Conversely, studies of wetting on grafted or absorbed polymer layers should provide a method to characterize their viscoelastic properties. Eventually, we discuss how structuring of copolymer films may influence their wetting properties and speculate about a possible link between the phenomena of viscoelastic braking<sup>i</sup> and task.<sup>ii</sup>

---

<sup>i</sup> a term coined out by Carre and Shanakan (in CRAS II, 1993, 317.1153 and Langmair 1995, 11, 24 and 1396) who in an elegant experiment have demonstrated that the spreading of a liquid on elastomers can be much slower than on rigid solids.

<sup>ii</sup> work done in collaboration with D. Long, A. Ajadari and A. Mourran

# Wetting and Mobility Characteristics of Thin Liquid Films of Perfluoropolyalkylether Lubricants on Solid Surfaces

Do Y. Yoon\*

IBM Almaden Research Center  
San Jose, CA 95120-6099

## Abstract

Thin films of perfluoropolyalkylethers of ca. 10 - 20 Å thickness play a very critical role as lubricants to prevent tribological failures at the head-disk interfaces of magnetic recording disk drives. As part of our efforts to better understand the effects of polymer structures on their tribological properties, we have investigated spreading characteristics of thin liquid films of perfluoropolyalkylethers on silica surfaces using scanning micro-ellipsometry. The polymer with nonfunctional chain ends spreads mainly by a diffusion-like movement of the fast moving front of less than 10 Å in thickness. The apparent diffusion constant of this front is nearly independent of the initial film thickness, and decreases with increasing molecular weight. In contrast, the polymers with functional groups at chain ends are found to spread by forming an apparent mono-molecular layer, the thickness of which increases with molecular weight. Moreover, this absorbed anchored layer separates out from the initial film layer, exhibiting the characteristics of wetting autophobicity. The surface mobilities of polymers with functional chain-end groups are dramatically lower than those of nonfunctional polymers in dry condition, but exhibits a very strong increase with relative humidity. Such an effect of humidity is not seen for the nonfunctional polymers. Furthermore, random copolymers are found to exhibit a higher surface mobility than those of homopolymers.

---

\* Work carried out in collaboration with B. G. Min, E. Lopez--Cabarcos, H. R. Brown, T. M. O'Connor, M. S. Jhon.

# Kinetics of Grafting Chains at Polymer Phase Boundaries: Implications for Compatibilization of Immiscible Polymer Alloys

Edward J. Kramer

Department of Materials Science and Engineering  
and the Materials Science Center  
Cornell University, Ithaca, NY 14853

## Abstract

Reaction of end-functional chains at polymer interfaces to form grafted chains is one strategy for compatibilization of polymer blends. Beyond decreasing the interfacial tension and the rate of particle coalescence, these grafted chains can reinforce the interface. In this talk I will review some of our recent experiments aimed at understanding the kinetics of such grafting, particularly the effects of the polymerization index  $N$  of the end-functional chains. If  $N$  is small, it is possible to achieve a large grafting density  $\Sigma$  relatively rapidly but such chains may not entangle effectively, leading to very weak interfaces. If  $N$  is large, a large  $\Sigma$  can be achieved and such chains are well enough entangled to support the growth of a wide craze, which strongly contributes to the fracture toughness. In modeling the kinetics two cases are considered: a case where the grafting is controlled by diffusion of free end-functional chains through the "brush" of previously grafted chains and a case where the grafting is controlled by the kinetics of the interface reaction itself. Both cases lead to the same form of the grafting kinetics, but with different characteristic times

$\tau_D = R_g a / D$ , where  $R_g$  is radius of gyration,  $a$ , the statistical segment length and  $D$ , the diffusion coefficient of the end-functional polymer, and  $\tau_R = R_g / (a k_f [B])$  where  $k_f$  is a forward rate constant and  $[B]$  is the concentration of groups at the interface that react with the end-function of the polymer chains.

## **Modeling the Behavior of Polymers Tethered at Impenetrable and Penetrable Interfaces**

**Anna C. Balazs**

Materials Science and Engineering Department  
University of Pittsburgh  
Pittsburgh, PA 15261

### **Abstract**

We show how various modeling techniques can be used to determine the properties of polymers tethered at impenetrable, solid surfaces and penetrable polymer/polymer interfaces. At solid surfaces, we use two dimensional self-consistent field theory and scaling arguments to investigate the self-assembly of end-grafted copolymers. The findings reveal a variety of novel structures that form with variations in the polymer-polymer, polymer-solvent and polymer-surface interaction energies. The results demonstrate how to use grafted chains to create thin films with well defined patterns.

For penetrable interfaces, we use Brownian dynamics simulations to simulate the fracture of a polymer/polymer interface that is reinforced by "connector" chains. The connectors weave back and forth across this boundary, forming either single or multiple "stitches". The work needed to fracture this interface is calculated as a function of the architecture and conformation of the connectors. The results show that the multi-stitch connectors dramatically improve the strength of the interface. This is rationalized through scaling arguments. The conclusions provide experimental guidelines for synthesizing effective connectors and thereby fabricating high-strength composites.

## **Structure-Property Relationships for Polymer Interphases in Fiber Reinforced Composite Materials**

**Lawrence T. Drzal**  
Departments of Chemical Engineering  
and Materials Science and Mechanics  
Michigan State University  
East Lansing, MI 48824-1326

### **Abstract**

When polymer composite materials are fabricated, polymer-reinforcing fiber interphases are formed which are critical elements necessary for optimal mechanical performance of composite materials. During composite processing, various chemical and physical mechanisms take place at the fiber surface in the formulated polymeric matrices which strongly influence the final interphase structure. For thermoset matrices, chemisorption of constituents, segregation of components, and processing constraints all can influence the resulting structure of the polymer in its solidified state. For thermoplastic matrices, segregation by molecular weight, morphological changes resulting from crystallization or additive segregation can also control the final matrix structure. In addition the surface of the fibers is coated with chemical agents that can also interact with the polymer. Examples will be given to illustrate the effect of the structure of this polymer interphase on adhesion. It will be shown that in some cases if the resulting polymer structure is known, adhesion and composite properties can be predicted.



### Abstract

Control of proteins and biomolecules at surfaces and interfaces is critical for a vast array of applications in technology and medicine including biomaterials, biofouling, protein separations, food processing, wastewater treatment, and the manipulations of genomic materials. Two broad subcategories associated with the control of proteins at surfaces are immobilizing protein when you want it, and preventing its attachment when you do not want it. Further issues are spatial control of proteins at surfaces, conformational stabilization and two-dimensional crystallization. This talk will cover surface modifications to enhance the protein adhesiveness, stabilize or alter conformation, and prevent adhesion. RF-Plasma deposited thin films will be emphasized. However, results will be presented with polyurethanes, self-assembled layers and LB films. Spatial control using an AFM will be described. Finally, methods to probe protein structure at interfaces including infrared spectroscopy, electron spectroscopy for chemical analysis (ESCA) and imaging time-of-flight secondary ion mass spectrometry (TOF-SIMS) will be discussed.

## Tethered Ligands for Controlling Cell Behavior

Linda G. Griffith-Cima  
MIT Department of Chemical Engineering  
Cambridge, MA

### Abstract

Much current research in biomaterials is directed toward covalently modifying materials with small peptide adhesion ligands to enhance cell adhesion and migration. There are at least two advantages to a complementary approach -- tethering ligands which are normally *soluble* and thus internalized and degraded by cells. One advantage is selectivity. We exploit this in making carbohydrate-modified materials for liver tissue engineering, in which we have demonstrated that cells attach, spread, and differentiate on surfaces bearing a simple carbohydrate ligand recognized by an hepatic-specific receptor, the asialoglycoprotein (ASGP) receptor. In this case, cellular response is governed by the mobility of the ligand on its "tether", polyethylene oxide (PEO). A second advantage in the case of ligands such as growth factors, which signal the cells to grow and migrate upon appropriate binding to a cell-surface receptor, is that a cell may respond in a more controlled fashion to a tethered ligand than to a soluble one. We have tethered epidermal growth factor (EGF) to a solid substrate in a manner permitting the factor to retain its biological activity as assessed by both mitogenic and morphological assays. Mouse EGF was covalently coupled to aminosilane-derivatized glass via star poly (ethylene oxide) (PEO), which allows the ligand to retain significant mobility and active conformation, unlike classical immobilization techniques. Tethered EGF was as effective as soluble EGF in eliciting DNA synthesis and cell rounding responses of primary rat hepatocytes under different surface conditions. In contrast, physically adsorbed EGF at comparable surface concentrations showed no activity. Presentation of growth factors in this manner may help to expedite their clinical use by permitting greater control of temporal and spatial availability in the extracellular environment.