

SYMPOSIUM FF
Electroactive Polymers

November 28 – December 1, 1999

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* Invited paper

TUTORIAL

FTF: ELECTROACTIVE POLYMERS (EAP) AS EMERGING ACTUATORS FOR DEVICES AND ROBOTIC APPLICATIONS

Sunday, November 28, 1999

1:30 - 5:00 p.m.

Room 206 (H)

This tutorial will provide an overview of the fundamentals of EAP and their application to actuators, devices, and robotic mechanisms and systems. The EAP materials that will be covered include ionic polymer metal composites, polymer gel, piezoelectric, electrostrictive, and electrostatic types. The basic mechanisms that are responsible for the electroactive behavior of EAP materials will be described. In addition, the mechanical properties of normal human muscle will be presented as the "gold standard" which is to be achieved by EAPs. The process of fabricating leading materials and methods of enhancing their performance will be reviewed. The fundamentals of EAP chemical and electrical stimulation will be covered and compared with natural muscle. The tutorial will also cover micro-fabricated sensors and actuators as related to the field of MEMS, which is a rapidly growing area. The tutorial will begin with a review of currently available EAP materials, which are also known as artificial muscles, their electroactivation mechanism and the principles of operating them as actuators. Capabilities, limitations, potentials and challenges to the application of EAP will be described. The tutorial will end with a description of the future prospects of EAP in space, industrial and medical devices/systems.

Instructors:

Yoseph Bar-Cohen, Jet Propulsion Laboratory

Paul Calvert, University of Arizona

Chang Liu, University of Illinois at Urbana-Champaign

Qiming Zhang, Pennsylvania State University

SESSION FF1:

Chairs: Jerry I. Scheinbeim and Qiming Zhang

Monday Morning, November 29, 1999

Simmons (M)

8:30 AM *FF1.1

ELECTROACTIVE POLYMERS: A SURVEY OF POTENTIAL APPLICATIONS. S.G. Wax, Defense Sciences Office, Defense Advanced Research Projects Agency; R. R. Sands, Washington, DC.

The field of Electroactive Polymers has experienced a considerable amount of expansion over the last decade. Much of this work has been concentrated on developing polymeric materials that behave like inorganic electronic materials or that mimic biological systems. This paper focuses on some of the nearer term applications that electroactive polymers might impact: actuators, sensors and light emitting polymers. Emphasis will be placed on potential actuator applications since these functions are of particular interest to the military. Performance metrics for existing actuators are compared to electroactive polymer actuators in an attempt to determine feasibility, and possible unique mechanical designs that take advantage of the intrinsic polymer behavior. In addition, mammalian muscle properties are compared to some of the observed polymer actuation properties.

9:00 AM *FF1.2

POLYMER ELECTROLYTE ACTUATOR DRIVEN BY LOW VOLTAGE. Keisuke Oguro, Kinji Asaka, Naoko Fujiwara, Osaka Natl Research Inst, Osaka, JAPAN; Kazuo Onishi, Shingo Sewa, Japan Chemical Innovation Inst, Osaka, JAPAN.

Composites of perfluorinated polymer electrolyte membrane and gold electrodes bend in response to low-voltage electric stimuli and work as soft actuators like muscles. The composites were prepared by the chemical plating method in which gold ions in the membrane were reduced at the surface of the membrane by aqueous solution of reducing agent. The chemical plating process leads to dendritic growth of gold electrodes on the surface of the membrane with large surface area which gives large capacitance, large current and large displacement even at low voltage around 2 V. Charging current to make electric double layer induces ion flux and electro-osmotic drag of water from anode to cathode through narrow channels in the perfluorinated ion-exchange resin. The electro-osmotic flow of water makes the resin near cathode wet and the resin near anode dry. The difference of water content swells or shrinks the resin and deflects the composite to anode. The actuator comprises polymer electrolyte, electrodes, counter ion, solvent, lead wires, etc. The performance of the actuator is affected by not only the components of the actuator, but also dimensions of the device, process of preparation, and

chemical or physical treatment of the membrane. Modification of these factors improved the performance and resulted in the deflection over 360 degrees at a film actuator of 10 mm long. The response is as quick as muscle. These actuators are applicable to artificial muscle, micro robots, or micro medical equipments inside body.

10:00 AM *FF1.3

CARBON NANOTUBE ARTIFICIAL MUSCLES AND SENSORS. Ray H. Baughman, Changxing Cui, Anvar A. Zakhidov and Zafar Iqbal, AlliedSignal Inc, Morristown, NJ; Joseph N. Barisci, Geoff M. Spinks, Gordon G. Wallace, University of Wollongong, Wollongong, AUSTRALIA; Alberto Mazzoldi and Danilo De Rossi, University of Pisa, ITALY; Andrew G. Rinzler, University of Florida, Gainesville, FL; Oliver Jaschinski and Siegmar Roth, Max Planck Institute, Stuttgart, GERMANY; Miklos Kertesz, Georgetown University, Washington, DC.

Electromechanical actuators based on sheets of single-wall carbon nanotubes are shown to provide higher stress generation capabilities than natural muscle, and higher strains than high modulus ferroelectrics. Both solid-state actuators and actuators that run in salt water are demonstrated and characterized. Like natural muscles, the macroscopic actuators are assemblies of billions of individual nano-scale actuators. The actuator mechanism (quantum-chemical-based expansion) does not require ion intercalation processes, which limit the life and rate of faradaic conducting polymer actuators. Low operating voltages of a few volts and high temperature capabilities are advantages compared with ferroelectrics. Predictions based on measurements suggest that nanotube actuators may eventually provide substantially higher work densities per cycle and higher stress generation capabilities than any previously known technology. Possible actuators based on carbon nanotubes range from large-scale devices, suitable for aircraft hydraulic systems, to microscopic and nanoscale devices. Also, these actuators can potentially be operated in reverse as mechanical sensors or for harvesting electrical energy from mechanical energy, such as the vibrations of aircraft or the motion of ocean waves.

10:30 AM FF1.4

CHALLENGES TO THE TRANSITION OF IPMC ARTIFICIAL MUSCLE ACTUATORS TO PRACTICAL APPLICATION.

Yoseph Bar-Cohen, Sean Leary, JPL/Caltech, Pasadena, CA; Keisuke Oguro, Osaka National Research Institute, Osaka, JAPAN; Satoshi Tadokoro, Dept. of Computer & Systems Eng., Kobe University, Kobe, JAPAN; Joycelyn Harrison, Joseph Smith and Ji Su, NASA LaRC, Hampton, VA.

Ion-exchange membrane metallic composites (IPMC), which were first reported in 1992, are one of the electroactive materials (EAP) with potential application as artificial muscle actuators. The recent introduction of perfluorocarboxylate-gold composite with tetra-n-butylammonium and Lithium cations instead of sodium made the most significant improvement of the material electroactivity. Under less than 3 volts, IPMC with the new constituents is capable of bending beyond a complete loop. Taking into account the fact that IPMC materials do not induce a significant force, the authors are extensively seeking applications for these bending EAP. Some of the applications that were demonstrated include dust-wiper, catheter guide, miniature motor, robotic-gripper, micro-manipulator, etc. Generally, space applications are the most demanding in terms of operating conditions, robustness and durability, and the co-authors of this paper are jointly addressing the related challenges. Specifically, a dust-wiper is being developed for the Nanorover's infrared camera window of the MUSES-CN mission. This is joint NASA and the NASDA (Japanese space agency) mission, is scheduled to be launch in January 2002 from Kagoshima, Japan, to explore the surface of a small near-Earth asteroid. Several issues that are critical to the operation of IPMC are addressed including the operation in vacuum, low temperatures, and the effect of the electromechanical characteristic of the IPMC on its actuation capability. Highly efficient IPMC materials, mechanical modeling, unique elements and protective coating were introduced by the authors and are making a high probability the success of the IPMC actuated dust-wiper.

10:45 AM FF1.5

HIGH DIELECTRIC CONSTANT POLYMER CERAMIC COMPOSITES. Yi Bai, V. Bharti, Z. -Y. Cheng, Haisheng Xu, Q.M. Zhang, The Pennsylvania State Univ, University Park, PA.

In the past several decades, there has been a great interest in the development of polymer ceramic composites, since they possess higher dielectric constants compared with polymers, while more flexibility and higher breakdown strength compared with ceramic. However, due to the low dielectric constant of polymer matrix, the relative dielectric constants of the composites developed up to date can only reach about 60. In this paper, we report a new polymer ceramic composite, in which the newly developed relaxor ferroelectric polymer with high

dielectric constant was used as the matrix. Different kinds of ceramic powders were studied and homogeneous composite thin films (20 μ m) were fabricated. It was observed that the increase of the dielectric constant of the composites with the ceramic content can be described quite well by the logarithmic mixing rule, when the ceramic content is below 60% by volume. The experimental data show that the relative dielectric constant of composites can reach higher than 250 with a flat temperature response (i.e., the dielectric constant changes little in a broad temperature range). In addition to high permittivity, the composite also have a high breakdown field strength (>150MV/m), which yields an energy storage density more than 20MJ/m³. The dielectric behavior of the composite at high frequency was also studied and the results show that the material is promising for microwave applications.

11:00 AM **FF1.6**

THE VOLTAGE AND COMPOSITION DEPENDENCE OF SWITCHING IN A POLYMER CURRENT LIMITER DEVICE.

Anil R. Duggal, GE Corporate Research and Development, Niskayuna, NY.

It has recently been demonstrated that certain conductor-filled polymer composite materials can be utilized as current-limiting elements to protect high power circuits from short-circuit events. Such polymer current limiter devices hold great potential for the circuit-protection industry since they can provide a new, nonmechanical way of rapidly limiting the destructive currents that can develop during fault conditions. However, the science behind the high power current-limiting phenomenon is not well understood. It involves polymer ablation and arc phenomena and depends sensitively on the polymer composite material properties. We present a qualitative model for operation and switching experiments as a function of voltage and material composition which support this model.

11:15 AM **FF1.7**

SMART POLYMER COMPOSITE THERMISTOR. Ralf Strümpler, Joachim Glatz-Reichenbach ABB Corporate Research, Baden-Dättwil, SWITZERLAND.

An industrially important class of passively smart materials are electrically nonlinear polymer composites. The transition of conducting composites from low to high resistivity can be utilized for current limitation. Due to Joule losses the material is heated by a fault or short-circuit current. With increasing temperature the polymer matrix expands and the current paths over the conducting filler particles are interrupted. Within milliseconds, the material responds to the fault current by an increase in resistivity up to eight orders of magnitude. Due to the strong nonlinear resistivity - temperature relation, a narrow hot-zone is formed even for long samples. The length of the hot-zone limits the maximum switching voltage. By adding a second filler material of varistor-type, however, the maximum voltage can be considerably increased. When a hot-spot is formed in one of the current paths over the conducting particles, a small voltage increase allows already a commutation of the current to neighboring varistor particles. Consequently, the current can still flow to a certain degree and allows to heat also the rest of the material around its path. This leads finally to a very broad hot area, which can resist much higher voltages. The length of the hot-zone is observed experimentally by an infra-red camera during the limitation of short circuit currents. By the development of a smart material with two strong non-linearities, a dramatic improvement has been achieved for the application of thermistor composites in current limitation.

11:30 AM **FF1.8**

LOWERING THE PERCOLATION THRESHOLD THROUGH POLYMER MICROSTRUCTURE. Jaime Grunlan, William Gerberich, Lorraine Francis, Univ of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN.

In an effort to lower the percolation threshold of carbon black-filled polymer composites, various polymer microstructures were examined. Composites were prepared with a polyvinyl acetate (PVAc) latex, a poly(vinyl acetate-ethylene) water-dispersible powder and a polyvinyl alcohol (PVA) as the matrix phase. Polymer microstructures were imaged using cryo-SEM techniques. Particulate microstructures (e.g., latex and dispersible powder) showed a significantly lowered percolation threshold relative to an equivalently prepared composite that utilized a solution-based matrix phase. The percolation threshold for the water-dispersible powder composite occurred at 5 vol.% carbon black and for the latex it was 3 vol.% carbon black, while the solution-based composite had a threshold of 14 vol.%. A four point probe apparatus was used to determine the locations of the percolation thresholds for each type of composite. By excluding the carbon black from regions occupied by polymeric particles, the dispersion-based composites create preferential aggregation of carbon black, as evidenced by SEM, and a lowered percolation threshold.

11:45 AM **FF1.9**

PHOTOCONDUCTIVE AND ELECTROCHROMIC POLYMER NANOCOMPOSITES AND DEVICES. Samson A. Jenekhe and Shujian Yi, University of Rochester, Department of Chemical Engineering, Rochester, NY.

Organic semiconductors such as metallophthalocyanines and perylenes are currently used as photoconductive elements in imaging technologies whereas conjugated polymers have promising photoelectronic properties for electrochromic displays, photodetectors, and solar cells. We have found that nanophase mixing of organic semiconductors with conjugated polymers results in new photoelectronic nanocomposite materials with tailorable electrochromic, photoconductive, and photoelectrochromic properties. Nanocomposites of metallophthalocyanines (MPC) with a conjugated polymer were found to contain spherical aggregates or rectangular nanocrystals of MPC dispersed in the matrix of the polymer. The binary MPC/polymer nanocomposites had excellent photoconductivity with near unity primary quantum yield and broad spectral response (300-900 nm). Photodetectors and electrochromic devices fabricated from the nanocomposites combined high sensitivity for radiation detection with good color contrast in electrochromic (EC) switching. For example, purple (neutral) \leftrightarrow yellow (-1 V, reduced) EC switching was observed at low MPC concentrations whereas blue (neutral) \leftrightarrow green (-1 V, reduced) EC switching of over 1,500 cycles was characteristic of the high concentration (>40% MPC) nanocomposites. The high photoconductivity of these same electrochromic nanocomposites throughout the visible and near infrared facilitated the exploration of various light-induced EC switching.

SESSION FF2:

Chairs: Takeo Furukawa and Jan F. Lindberg
Monday Afternoon, November 29, 1999
Simmons (M)

1:30 PM ***FF2.1**

STRUCTURE, PROPERTIES, AND APPLICATIONS OF SINGLE CRYSTALLINE FILMS OF VINYLIDENE FLUORIDE AND TRIFLUOROETHYLENE COPOLYMERS. Hiroji Ohigashi, Yamagata Univ, Dept of Materials Science and Engineering, Yonezawa, JAPAN.

The single crystalline (SC) film of P(VDF/TrFE) (copolymer of vinylidene fluoride and trifluoroethylene), is a highly crystallized, highly double-oriented, and optically transparent ferroelectric film, which can be prepared by crystallizing a uniaxially drawn film in the paraelectric phase with its ends being clamped and its surfaces leaving free. The SC film is composed of endlessly extended chain crystals whose c-axis aligns along the stretching direction almost perfectly and the polar b-axis orients $\pm\psi/6$ off the film normal. It does not contain lamellar crystals nor amorphous phase. Owing to such unique structure, the SC film exhibits the ferroelectricity and related properties inherent to the crystal more clearly than the films composed of lamellar crystals. In this paper, we present our recent studies on the SC films: (1) the structure and morphology revealed by POM, TEM, and X-ray diffractions; (2) the ferroelectric, piezoelectric, mechanical, and optical properties in the ferroelectric phase; (3) motions of molecular chains in the paraelectric phase as revealed by dielectric, X-rays and shear mechanical studies; and (4) applications to shear ultrasonic transducers. The followings are the main results to be emphasized. (A) The SC film has a large Young's modulus (120GPa at 10K) in the direction along the stretching axis. (B) The SC film is the most effective piezoelectric polymer film among any other poled polymer films ever reported. The film also exhibits a large Pockels effect. (C) In the paraelectric phase, the crystal is a liquid crystal of 1D-liquid and 2D-solid, and in the crystal, each molecular chain of TGTG' conformation undergoes rotational and flip-flop motions independently of neighboring chains in the highly regular hexagonal crystal lattice. Anomalous dielectric behavior observed is attributed to these molecular motions. (D) SC film transducers for shear ultrasonic waves are effectively used in NDE.

2:00 PM ***FF2.2**

STRUCTURAL CHANGE IN FERROELECTRIC PHASE TRANSITION OF VINYLIDENE FLUORIDE COPOLYMERS AS STUDIED BY WAXS, SAXS, IR, RAMAN, AND COMPUTER SIMULATION TECHNIQUES. Kohji Tashiro, Osaka University, Graduate School of Science, Osaka, JAPAN.

In a series of papers we reported that the molecular chains experience the remarkable conformational changes between trans and gauche forms in the ferroelectric phase transition of vinylidene fluoride-trifluoroethylene copolymers. The packing structure of these chains is also changed drastically. In the first half part of this presentation, the structure change in the crystalline region is

simulated by carrying out the molecular dynamics calculation and the various important factors governing the phase transition are extracted. Through the measurement of the temperature dependence of wide-angle X-ray scattering and small-angle X-ray scattering, the morphology or the aggregation structure of crystallites was found to change drastically in this transition. An intimate relationship between the structure change in the crystallite and the change in the morphology was discussed in the second half part of this paper.

2:30 PM **FF2.3**

EFFECT OF PROCESSING AND HIGH-ENERGY ELECTRON IRRADIATION CONDITIONS ON THE ELECTRO-MECHANICAL AND STRUCTURAL PROPERTIES OF P(VDF-TRFE) COPOLYMER FILMS. V. Bharti, Z.-Y. Cheng, Haisheng Xu, G. Shanthi, T.-B. Xu, Q.M. Zhang, The Pennsylvania State Univ, University Park, PA.

Recently it has been demonstrated that using a high electron energy irradiation, the electro-mechanical properties of poly(vinylidene fluoride - trifluoroethylene, P(VDF-TrFE) copolymers can be improved significantly. For example high electric field induced strain (~4.5%) with high elastic energy density, high dielectric constant (~65 with loss less than at 1kHz), high piezoelectric coefficient (~350 pm/V) and high electro-mechanical coupling coefficient (~0.42) have been observed. It was found that depending on sample processing and electron irradiation conditions these properties can be tailored over a wide range. In this talk we will present the experimental data on the effect of processing and irradiation conditions on structural and transitional behavior of copolymers. The structural information will be coupled with the electro-mechanical properties to provide understanding on what are responsible for the observed phenomena and how the properties can be improved further. In addition we will highlight some experimental evidence that strain induced in this copolymer system is mainly due to local phase switching instead of Maxwell stress effect as has been observed in other polymeric materials.

2:45 PM **FF2.4**

SYNTHESIS AND ELECTRIC PROPERTIES OF POLY(VDF/TRFE/HFP) TERPOLYMERS. Atitsa Petchsuk, T.C. Mike Chung, The Pennsylvania State Univ, Dept of Materials Science, University Park, PA.

This presentation will discuss a new synthesis route to prepare poly(VDF/TrFE/HFP) terpolymers containing vinylidene difluoride, trifluoroethylene and hexafluoro-1-propene units. The new low temperature initiation system and homogeneous reaction conditions allow the formation of soluble and melt-processible terpolymers with a broad range of terpolymer composition, high molecular weight, and narrow composition distribution. In addition, the low temperature reaction conditions also provide an excellent control of regio-selectivity (head-to-tail sequences) during the incorporation of monomers. The combination of DSC, optical polarized microscopy and x-ray results show the detailed composition-microstructure relationships in terpolymers. In general, the terpolymer having low concentration of HFP units shows high crystallinity and low Curie transition temperature. The small amount of HFP units homogeneously distributed along the VDF/TrFE (60/40 mole ratio) polymer chain effectively reduces the crystal size and changes the Curie temperature to near room temperature, and only has a small effect to the overall crystallinity. In parallel, the electromechanical properties of the terpolymers having good processibility, high crystallinity and low Curie temperature are evaluated by Zhang's group at PSU. The results will also be discussed during this presentation.

3:30 PM ***FF2.5**

GIANT ELECTROSTRICTIVE RESPONSE IN POLY(VINYLIDENE-FLUORIDE HEXAFLUOROPROPYLENE) COPOLYMER. Xiaoyan Lu, Adriana Schirokauer, Rutgers University, Dept of Chemical and Biochemical Engineering, Piscataway, NJ.

Electrostrictive strains are known to be proportional to the square of the applied field. Materials exhibiting large strains offer great promise in applications such as sensors, actuators, artificial muscle, robotics and MEMS. Previous studies [1] found large electrostrictive strains (> 3%) in a low modulus polyurethane thermoplastic elastomer. In a recent work, [2], field-induced strains were investigated in poly(vinylidene-fluoride trifluoroethylene) copolymers. The materials exhibited electrostrictive strains of approximately 4% under electric fields of 150 MV/m for films irradiated with a high energy electron beam. In the present study, the strain response of a new class of copolymers of PVF2 is investigated. Electrostrictive strains were measured in poly(vinylidene-fluoride hexafluoropropylene), P(VF2-HFP), under electric fields up to 60 MV/m. Melt pressed samples were prepared with two different HFP content; 15% and 5% HFP. Electrostrictive strains were measured, using a capacitance method (air-gap capacitor), as a function of electric field. Ice water

quenched undrawn samples exhibited the largest response in both compositions. Strains greater than 4% were observed in the 5% HFP quenched P(VF2-HFP) copolymer. Following the same behavior, 15% HFP quenched films showed the largest strains (~3%). Values of elastic modulus were lower for the quenched 5% films than for the slow cooled ones, and in both cases they were higher than the previously studied polyurethane elastomers and poly(vinylidene-fluoride trifluoroethylene) copolymers. References: [1] Ma, Z., J. Scheinbeim, J. Lee and B. Newman. High Field Electrostrictive Response of Polymers. *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 32, 2721-2731(1994). [2] Zhang, Q. M., V. Bharti and X. Zhao. Giant Electrostriction and Relaxor Ferroelectric Behavior in Electron-Irradiated Poly(vinylidene fluoride-trifluoroethylene) Copolymer. *Science*, Vol. 280, 2101-2104 (1998).

4:00 PM **FF2.6**

ELECTRO-MECHANICAL PROPERTIES OF ELECTRON IRRADIATED POLY(VINYLIDENE FLUORIDE-TRIFLUOROETHYLENE) COPOLYMERS. Z.-Y. Cheng, S. Gross, V. Bharti, T.-B. Xu, Q.M. Zhang, The Pennsylvania State Univ, University Park, PA.

Recently it was reported that large transverse and longitudinal electrostrictive strain responses can be achieved in high energy electron irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer films [1,2,3]. Being a polymeric material, the mechanical load ability is always a concern, which is crucial for many device applications. In this paper, the electric induced transverse strain response of the material under uniaxial mechanical load is investigated over a broad range (from 0 to 45 MPa) and it is found that the strain response of the films under a given electric field increases first and then decreases with load and as a result, the field induced strain under 45 MPa is the same as that under load stress condition. The longitudinal strain response of the materials under hydrostatic pressure is also studied. The strain responses show slight rise with the pressure. In order to understand these stress dependent behaviors in particular and the micro-mechanism of the field induced strain of this class of new material in general, the volume strain of the material is measured. It is shown that the strain response of the copolymer films originates mainly from the electric field induced phase transformation of the local polar regions. Based on this result and the phenomenological theory, the load dependence of the strain response can be understood through the shift of local Curie temperatures with the mechanical load. The work was supported by ONR through Grant No. N00014-97-1-0900, NSF through Grant No. ECS-9710459, and DARPA through Grant No. N00173-99-C-2003. [1]. Q.M. Zhang, et al., *Science* 280, 2101 (1998). [2]. X. Zhao, et al., *Appl. Phys. Lett.* 73, 2054 (1998). [3]. Z.-Y. Cheng, et al., *Appl. Phys. Lett.* 74, 1901(1999).

4:15 PM **FF2.7**

POLARIZATION DISTRIBUTION IN ELECTRON-IRRADIATED COPOLYMER OF VINYLIDENE FLUORIDE AND TRIFLUOROETHYLENE (50/50 WEIGHT PERCENT).

Aime S. DeReggi, Polymers Div., NIST, Gaithersburg, MD; Edward Balizer, NSWC/Carderock Div., West Bethesda, MD; Fred Bateman, Radiation Physics Div., NIST, Gaithersburg, MD; Dan A. Neumann, Center for Neutron Research, NIST, Gaithersburg, MD.

The polarization distribution in the 50 wt.% vinylidene fluoride-50 wt.% trifluoroethylene copolymer, a composition that was first reported to show large electrostriction after irradiation (Zhang, Bharti, Zhao, *SCIENCE*, Vol. 283, p. 2101, 1998), has been studied by the thermal pulse method before and after 1 MeV primary electron irradiation under various combinations of temperature and dose. The effects of collateral lower energy secondary electron irradiation due to back scattering from the bottom of the Al irradiation chamber were considered. The thermal pulse measurements were coordinated with differential scanning calorimetry measurements to establish the radiation effects on the crystallinity and the Curie transition, and with neutron scattering measurements to establish the effects of a high applied electric field on the structure.

4:30 PM **FF2.8**

ELECTRON IRRADIATED P(VDF-TrFE) COPOLYMERS FOR USE IN NAVAL TRANSDUCER APPLICATIONS. K.E. Hamilton¹, T. Ramotowski¹, G. Kavarnos¹, Q. Zhang², V. Bharti²; ¹Transducer Material Branch, Naval Undersea Warfare Center, ²Materials Research Laboratory, The Pennsylvania State University..

Recently, it was discovered that the transduction / strain capability of P(VDF-TrFE) copolymer materials can be enhanced by more than an order of magnitude by irradiating with large doses (40-300 Mrad) of β -particles (1-3 MeV electrons). The goal of this project is to understand the role of the irradiation process in improving the electromechanical properties (electrostrictive, piezoelectric, or otherwise) while simultaneously identifying the secondary effects of irradiation on the material (not critical to the electromechanical

properties), and attempting to separate the two contributions. It has been found that the irradiation processing affects the material profoundly in several different manners. Reduction in melt temperature, degree of crystallinity, and the resulting crystal quality have been observed with increasing doses of β -particles. Similar results have been observed for the Curie transition temperature, the energy associated with that transition, and the changes in the transition breadth. Dielectric constant measurements over wide temperature and frequency ranges have reflected some of these morphological changes. In addition, thermogravimetric analysis indicates that irradiation results in both chain scission and network polymer formation. Findings from solid-state NMR characterization will be discussed in reference to the postulated dehalogenation, dehydrohalogenation, and olefinic bond formation activities.

4:45 PM FF2.9

DYNAMICS OF PYROELECTRICITY OF A COPOLYMER OF VINYLIDENE FLUORIDE WITH TRIFLUOROETHYLENE.

Yoshiyuki Takahashi, Junichi Taniwaki, Takeo Furukawa, Science Univ of Tokyo, Dept of Chemistry, Tokyo, JAPAN.

The pyroelectric response curve is obtained by irradiating a laser pulse to a poled film through a transparent electrode and measuring the charge response of the sample as a function of time^{1,2}. In this paper, we report the pyroelectric response curves of a copolymer of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) with VDF content of 75 mol% supplied by Daikin Industries, Ltd. The polymer film was cast from dimethylformamide solution with crystal violet as a dye. The film was annealed at 145°C for 1 hour and gold was evaporated on both surfaces as electrodes. After poling by an ac field of 100MV/m, the gold electrodes were wiped out and the film was put between two glass slides that were coated with indium-tin oxide as transparent electrodes. The film was irradiated by a laser pulse of the second harmonic of YAG. As crystal violet absorbs the light, the sample film was assumed to be heated uniformly. The charge response was measured as a function of time in a range of 1ns to 10s. The temperature was varied from room temperature to 130°C. The pyroelectric response curve is found to be composed of several processes. Abrupt thermal expansion induces mechanical oscillations of proper frequencies corresponding to the dimensions of the sample. Being coupled with piezoelectricity such mechanical oscillations result in oscillations in the pyroelectric response curve. As temperature is raised above 100°C, slow process is found around 10⁻³s up to 115°C, above which the pyroelectricity begins to be lost due to the Curie transition. Because the slow process appears near below T_C , it is supposed to correspond to some leading process of the transition.

¹ R.G. Kepler and R.A. Anderson, *Mol. Cryst. Liq. Cryst.*, **106**, 345, (1984)

² Y. Takahashi, K. Hiraoka and T. Furukawa, *IEEE Trans. Dielec. Electr. Insul.*, **5**, 957, (1998)

SESSION FF3: POSTER SESSION
Chair: Zhong-Yang Cheng
Monday Evening, November 29, 1999
8:00 P.M.
Exhibition Hall D (H)

FF3.1

PIEZOELECTRIC AND MECHANICAL PROPERTIES OF HUMAN AND BOVINE CORNEA. Ambalangodage C. Jayasuriya, Jerry I. Scheinbeim, Polymer Electroprocessing Laboratory, Dept of Chemical and Biochemical Engineering, Rutgers, The State Univ of New Jersey, Piscataway, NJ; Virginia Lubkin, Greg Bennett, Aborn Laboratory, New York Eye and Ear Infirmary, New York, NY.

Piezoelectricity has been investigated for many different biological materials such as bone, tendon, muscle and skin. (1) In a previous study we found significant piezoelectricity in human eye sclera. (2) In the present study, we report the (tensile) piezoelectric coefficient (d31) and Young's modulus for both human and bovine eye corneas. The d31 coefficient and modulus were measured simultaneously at room temperature. For samples cut at 45° to the horizontal, an extremely large d31 coefficient of 2200 pC/N was observed for both kinds of corneas. This value is extremely large compared with that of any synthetic organic polymer. The measured modulus was between 0.1-3 MPa for human and bovine corneas, depending on direction. The piezoelectric and mechanical responses observed were anisotropic for both kinds of corneas and d31 coefficient decreased, while modulus increased with dehydration time. The structure of these materials is complex with collagen, providing the majority of the tensile strength. The polar nature is due to the 3.7 Debye dipole moment of the peptide unit. The water molecules in the collagen play a major roll for both piezoelectric and mechanical properties of both types of corneas. According to WAXD and FTIR measurements, water molecules appear to increase crystallinity of collagen in the corneas. The

piezoelectric response observed may be attributed mainly to N-H and C=O dipoles in the crystalline regions of the collagen. The observed anisotropic behavior of corneas is likely due to oriented crystalline collagen fibrils. References: (1). E. Fukada, *Advan. In Biophys.*, **6**, 121-155 (1974). (2). S. Ghosh, B. Z. Mei, V. Lubkin, J. I. Scheinbeim, B. A. Newman, P. Kramer, G. Bennett and N. Feit, *J. Biomed. Mate. Res.*, **39**, 453-457 (1998).

FF3.2

ELECTROCHEMICAL CHARACTERIZATION OF POLY-ANILINE(PANI)/THIOLKOL RUBBER(TR) FILMS AS ELECTRODE MATERIAL.

Jia Zhenbin, Ding Keqiang, Zhao Qian, Tong Ruting, Hebei Teachers' Univ, Dept of Chemistry, Shijiazhuang, CHINA.

Organodisulfides compound is one higher energy material for the secondary battery. The redox reaction of cysteine/ cystine was studied in the sulphuric acid on the PANI/TR electrode using cyclic voltammetry (CV) and electrochemical impedance spectroscopy(EIS). The using of PANI/TR electrode has changed the E(Pa-Pc) of the redox peaks potentials on the Pt electrode from 744mV to 282 mV. The reduction current is increased markedly, the current ratio of the redox reaction approximates 1. One pair nearly reversible peaks appears. The EIS closely approximate the response of a finite transmission line with an approximately 45° linear region (Warburg-type region) at high frequency giving way to an almost 90° linear region at low frequency, which confirmed the higher conductivity, electroactivity and stability of the film even after being immersed in the cysteine sulphuric acid solution for several days. The results we obtained are in accordance with the earlier conclusion that PANI could electrocatalyse the reaction containing s-s bonds. What's more, the electrocatalytic function of the PANI/TR film is much more significantly than the single PANI electrode. Some effective conditions on the films have also been considered. In the above system, we could observe that both the reversibility and current are increased on the PANI/TR electrode.

FF3.3

X-RAY DIFFRACTION AND IR SPECTROSCOPIC STUDIES OF NICKEL CHLORIDE POLY(ETHYLENE OXIDE) SOLID FILM MATERIAL. Bixia Huang, Jun Yue, University of Science and Technology of China, School of Chemistry and Material Science, Dept of Chemistry, Hefei, P.R. CHINA; Yue Xiaohui, Auburn University, Dept of Chemistry, Auburn, AL.

A number of PEO-based materials exhibit substantial ionic conductivity, which implies the possibility of potential application as solid electrolytes. In the present study, with double solvents method, a series of NiCl₂(PEO)_n (n= 4-24) solid film materials were prepared and their morphology and hydration were investigated in detail by use of X-Ray Diffraction and Infrared Spectroscopy. It showed that all NiCl₂(PEO)_n systems consist of multiple phases, including crystalline PEO, crystalline complex of PEO with dissolved nickel salts, and crystalline compounds formed between solvent (DMSO) and salts. Hydration destroys crystalline compounds of both PEO and DMSO with nickel salts. The IR bond of ether oxygen coordinated to nickel ion shifts to higher wave number due to hydration, implying a weakening interaction between PEO and hydrous nickel ions. Annealing procedure only re-builds crystalline complex phase of PEO with nickel salts of which crystallinity diminishes due to hydration/dehydration. The effect of salt concentration on structure and hydration/dehydration of PEO based polymeric materials was discussed.

FF3.4

STRUCTURAL AND QUANTUM MECHANICS ANALYSIS OF POLYANILINE + CuII. Jorge A. Ascencio, Instituto Nacional de Investigaciones Nucleares, MEXICO; R. Lopez-Castarez, O. Olea-Cardoso, Universidad Autonoma del Estado de Mexico, MEXICO.

The last decades have been characterized by the application of simulation and computational techniques to the different application in all the science field. In particular, the molecular simulation have become really important in the materials science because the possibilities of study the theoretical principles in a relatively easy way. Besides, optical and electronic properties in polymers are well identified as one of the most important applications of ductile materials. In this case, polymers doped with metals have shown excellent perspectives, however the theoretical analysis is not actually enough. So, in order to identify the structural configuration and the main molecular and atomic properties of the polymer a Density Functional Approximation is applied to find a geometry optimization and to analyze the local conditions of the polyaniline structure, which is doped with CuII to introduce changes in its electrical properties. The analysis is made in the original molecule and when it is doped with CuII to identify the preferential atoms in the macromolecule to

receive the Cu atoms. In the same way the energy minimization is used to identify the optimal configuration and to study their charge distribution which affects to its macroscopic properties.

FF3.5

IN SITU CONDUCTIVITY OF THE POLY(3,4-ETHYLENE-DIOXYTHIOPHENE) ELECTROSYNTHESISED IN AQUEOUS SOLUTIONS IN THE PRESENCE OF LARGE ANIONS.

H.J. Ahonen, Jukka Lukkari, Jouko Kankare, Univ of Turku, Dept of Chemistry, Turku, FINLAND.

We have polymerised 3,4-ethylenedioxythiophene (EDOT) in the presence of micelle forming sodiumdodecylsulfate (SDS) and some other large non-micelle forming anions in aqueous solutions, and compared their in situ conductivity to the films prepared in the presence of small anions. Sakmeche et al. has previously reported the possible increase of order in the film polymerised in the presence of micelle forming SDS [1]. Ordering in the film is usually connected to high mobility of charge carriers and, therefore, high conductivity of the sample. In spite of the supposed increased order in these films, the measured in situ conductivity is more than two orders of magnitude higher in the films polymerised in the presence of small hexa-fluorophosphate anion. In addition, the conductivity of the films prepared in the presence of non-micelle forming picrate or tosylate anions was in the same order as the conductivity of the films polymerised in the presence of SDS. These results suggest that some other factor than order in the film determines the measured in situ conductivity in this case. Furthermore, all the films polymerised in any aqueous solution had inferior in situ conductivity to the films prepared in anhydrous acetonitrile. This behaviour can be related to the hydrophilic nature of the polymer in oxidised state. During the galvanostatic or potentiostatic polymerisation the polymer chains attached to the electrode are kept constantly in the oxidised state, thus being hydrophilic and letting the water molecules penetrate and reside in the forming film. This would lead to a more swollen polymer film compared to the films polymerised in anhydrous acetonitrile. In more swollen polymer, the concentration of the charge carriers is smaller and interchain hopping less favoured, which leads to a smaller conductivity. [1] Sakmeche N., Aeiyaeh S., Aaron J. -J., Jouini M., Lacroix J. C. and Lacaze P.-C. Langmuir, 1999, 15, 2566-2574.

FF3.6

DIELECTRIC RELAXATION SPECTROSCOPIC STUDIES ON ELECTROACTIVE POLYMERS. S. Abdul-Jawad, A. An-Najjar, Dept. of Physics, UAE University, Al-Ain, UAE; **Mamoun M. Bader**, Dept. of Chemistry, Penn State Univ, Hazleton, PA.

Results of our dielectric relaxation spectroscopic measurements in the frequency range 1Hz - 1MHz and over a wide temperature range on two electroactive polymers will be presented. The polymers studied were: electro polymerized polypyrrole and a side chain electro-optic polyimide. The effect of the introduction of ionic impurities in these polymeric materials (which is most likely to be the case) on the dielectric characteristics of these materials will be presented. In addition, temperature effects on the dielectric properties will be addressed. The activation energy for the rotation of the side chain chromophore is estimated based on these temperature dependence studies.

FF3.7

PREPARATION AND CHARACTERIZATION OF LIQUID CRYSTALLINE CONDUCTING POLYANILINE.

Somkiat Piankijesakul, Kalle Levon, Department of Chemistry, Chemical Engineering and Materials Science, Polytechnic University, NY.

Liquid crystalline conducting polymers have attracted much attention because higher conductivity can be attained by alignment of conjugated chains. However, liquid crystals in polyaniline have scarcely investigated due to its solubility and rigidity. Recently, lyotropic liquid crystalline polyaniline was successfully prepared in our laboratory. In this study, thermotropic liquid crystalline trianiline was synthesized and used as a model compound to study liquid crystalline behaviors in polyaniline. Liquid crystallinity was induced by complexation of trianiline and various amount of a mesogenic dopant, 10-(4-(4'-n-butyl)azobenzenoxy)decanesulfonic acid (BABDSA). Polarizing microscope studies demonstrated that the complexes exhibited a focal conic fan texture which is typical aligned smectic A phase, when cooling an isotropic phase. DSC studies revealed the anisotropic transition temperature in complexes. Moreover, UV-visible measurements showed that the increasing amount of BABDSA decreased the absorption of the quinoid ring excitation at 580 nm and increased the absorption of polaronic transition at 800 nm. Furthermore, the change in the intensity ratio of peaks at 1600 cm^{-1} and 1500 cm^{-1} in FT-IR is the evidence for the protonic process. X-ray diffraction analyses indicated that all of complexes showed inter-layer and side-chain diffractions in the liquid crystal states.

FF3.8

FAST PROTON CONDUCTORS FROM INORGANIC-ORGANIC COMPOSITES : I. AMORPHOUS P_2O_5 / ION-EXCHANGE RESIN. Yong-il Park and Masayuki Nagai, Department of Energy Science and Technology, Musashi Institute of Technology, Tokyo, JAPAN.

A drastic increase of electrical conductivity was observed in the composite thin films of amorphous phosphorus oxide and ion-exchange resin as phosphorus concentration increased. Incorporation of P_2O_5 glass into a sulfonated polymer, Nafion, caused a large increase of electrical conductivity to about 0.75Scm^{-1} at 22°C . Some other polymers were also used as matrices and their electrical conductivity were characterized to compare with the electrical conductivity of P_2O_5 /Nafion composite. Effects of heat-treatment temperature and humidity on electrical conductivity and chemical stability were also investigated.

FF3.9

FAST PROTON CONDUCTORS FROM INORGANIC-ORGANIC COMPOSITES : II. AMORPHOUS ZrO_2 - P_2O_5 / POLYMER.

Yong-il Park and Masayuki Nagai, Department of Energy Science and Technology, Musashi Institute of Technology, Tokyo, JAPAN.

Thin films of amorphous zirconium phosphate/polymer composites were fabricated on glass substrates through sol-gel spin-coating. The polymer was incorporated to provide mechanical stability and flexibility, whereas the ZrO_2 - P_2O_5 amorphous electrolyte provides a passway for proton transport. An increase of electrical conductivity was observed in the obtained films with increasing zirconium phosphate content at room temperature. Thermal stabilization of composite films by inducing zirconium phosphate was characterized, and the effects of heat-treatment temperature and humidity on electrical conductivity and chemical stability were also investigated.

FF3.10

Abstract Withdrawn.

FF3.11

ANALYSIS OF FERROELECTRIC SWITCHING PROCESS IN VDF/TrFE COPOLYMERS. Kenji Kano, Hidekazu Kodama,

Yoshiyuki Takahashi, Takeo Furukawa, Science Univ. of Tokyo, Dept. of Chemistry, Tokyo, JAPAN.

Vinylidene fluoride (VDF)/trifluoroethylene (TrFE) copolymers exhibit fast polarization switching when a step-wise high electric field is applied in the direction opposite to the existing remanent polarization. We have previously shown that the observed switching curve consists of two processes, an initial gradual increase in proportion to $t^{0.5}$ followed by a rapid increase according to $1 - \exp(-(t/\tau)^n)$ with large exponent $n = 6$. Such a two-step character and an unrealistic large exponent are beyond the prediction of the conventional nucleation-growth theory. We have undertaken computer simulation to reproduce the observed switching curve. We prepared an array of N (1D-growth) or $N \times N$ (2D-growth) cells and assign S to a cell to describe its polarization state. S is assigned to be 0 before switching and S_c after switching. When a cell is chosen to be a nucleation site according to probability R , its S value is subjected to $+1$ or -1 increment randomly at every simulation step. Once S reaches S_c , the chosen cell becomes a nucleus and induces the switching of adjacent cells by changing their states from 0 to S_c at the next step. Computing a sum of S of all cells at every simulation step yields the time evolution of switching process. It was found that the observed switching curve can be well-reproduced by choosing an appropriate set of R and S_c values with respect to a heterogeneous nucleation system. It is concluded that the initial gradual increase corresponds to nucleation that progresses as a random walk and the following rapid increase is attributed to a growth process that starts after completion of nucleation (induction time).

FF3.12

FERROELECTRIC AND ANTIFERROELECTRIC PHASE TRANSITIONS IN VDF/TrFE COPOLYMERS. H. Kodama, Y.

Takahashi and T. Furukawa, Science Univ. of Tokyo, Dept. of Chemistry, Tokyo, JAPAN.

Copolymers of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) containing 50-80mol% former exhibit a transition from a ferroelectric all-trans phase to a paraelectric motional phase as demonstrated by loss of remanent polarization, dielectric anomaly and anomalous specific heat. The value of transition entropy is consistent with conformational disorder under a constraint that molecules remain linear. As the VDF content becomes larger than 80mol%, the ferroelectric transition is overtaken by melting. On the other hand, when the TrFE becomes the major component, ferroelectricity tends to be obscured to disappear in PTrFE. In the range of 30 - 50mol% VDF content, an additional phase appears between the ferroelectric

and paraelectric phases. This new phase is non-polar as well as non-motional and can be characterized as being antiferroelectric-like on the basis of its double hysteresis nature. In the present paper, we summarize the transition behavior of VDF/TrFE copolymers over the entire range of composition in terms of transition temperature, transition entropy and enthalpy, remanent polarization and lattice spacings, and discuss the role of TrFE in the ferroelectric nature of VDF copolymers.

FF3.13

STRUCTURE AND PROPERTIES OF EXTRUSION DRAWN POLY(VINYLDENE FLUORIDE). Koh Nakamura, Masayuki Nagai, Tetsuo Kanamoto, Yoshiyuki Takahashi, Takeo Furukawa, Science Univ. of Tokyo, Faculty of Science, Tokyo, JAPAN.

It has been shown that the limiting electrical properties for vinylidene fluoride (VDF)/trifluoroethylene (TrFE) copolymers depend on the VDF contents, and the poly(vinylidene fluoride) (PVDF) homopolymer has theoretically the highest remanent polarization and piezoelectricity. Oriented PVDF films with β -form crystals have been commonly prepared by cold-drawing of a melt-quenched film, consisting of α -form crystals. In this study, we have successfully produced highly oriented PVDF thin films, 20 μm thick, with β -crystals and a high crystallinity, by solid-state coextrusion of a gel film consisting of α -form crystals to 9 times the original length at an optimum extrusion temperature of 160°C, some 10°C below the melting temperature. The resultant drawn film with an extrusion draw ratio of 9 had a highly oriented fibrous structure ($f_c=0.992$), and showed improved mechanical and electrical properties; an elastic modulus along the draw direction of 10.5 GPa, a remanent polarization of 100 mCm^{-2} , and an electromechanical coupling coefficient in the TE (thickness-extensional) mode, k_t , of 0.27. These values are the highest among those ever reported for β -PVDF films. When the chains of β -crystals are oriented parallel to the draw axis, it is assumed that P_r is proportional to the sample crystallinity. Thus a crystallinity value of 80 % was estimated for the extrudate having a high chain orientation, based on the ratio of the observed P_r to the theoretical P_r of 126 mCm^{-2} . This fact revealed that even when the deformation was made near the melting temperature, highly oriented and highly crystallinity β -form films with superior mechanical and electrical properties were produced from the α -form by deformation in the shear and extensional flow fields under a high pressure. The morphology of the extrudate relevant to such properties will be discussed.

FF3.14

FERROELECTRIC AND PIEZOELECTRIC PROPERTIES OF BLENDS OF POLY(VINYLDENE-TRIFLUOROETHYLENE) AND GRAFT ELASTOMER. Ji Su, National Research Council, Zoubeida Ounaies (ICASE) and Joycelyn S. Harrison, NASA Langley Research Center, Hampton, VA.

A two component, three phase molecular composite system has been developed. The system contains ferroelectric poly(vinylidene-trifluoroethylene) and electrostrictive plastic grafted elastomer. The ferroelectric and piezoelectric properties of the blends have been studied as functions of temperature and frequency. The molecular structure and the effects of the electrical poling treatment on the structure have also been investigated using x-ray diffraction and differential scanning calorimeter (DSC) techniques. The work will present (1) the dependence of the molecular structure and morphology in the system on the sample preparation, especially the thermal history and mechanical stretching; (2) the remanent polarization, P_r , and the piezoelectric coefficient, d_{31} , of the composite system as a function of fraction of the ferroelectric copolymer in the system; and (3) the effects of the thermal treatment and mechanical orientation on the macroscopic properties such as the dielectric constant, the remanent polarization, and the piezoelectric coefficient. The interrelationship of processing, structure, and properties will also be discussed.

FF3.15

COMPUTER CONTROLLED PULSED PECVD REACTOR FOR LABORATORY SCALE DEPOSITION OF PLASMA POLYMERIZED THIN FILMS. P. Pedrow, Washington State University, School of Electrical Engineering and Computer Science, Washington State University, Pullman, WA; L. Shepsis and R. Mahalingam, Department of Chemical Engineering, Pullman, WA; M. Osman, School of Electrical Engineering and Computer Science, Washington State University, Pullman, WA.

A pulsed PECVD reactor has been constructed for laboratory scale studies of plasma polymerized thin films. Substrates with diameter as large as 10 cm can be accommodated. Both liquid phase and gas phase feedstock can be introduced into the reactor from a multiplicity of injector valves. A computer control system based on National Instrument's LABVIEW software controls power supply sequence,

feedstock injection, and introduction of RF energy. The pulsed nature of the reactor minimizes consumption of feed stock and facilitates the creation of thin composite films. Deposition rates can be controlled precisely within the range 10 to 60 angstroms per pulse. Repetition rate can be as high as 2 pulses per minute. Optical fiber and a photo diode allow the user to monitor emitted light for each pulse. Monomers used to date in this reactor include acetylene, ethylene, and aniline. The reactor design allows the user to introduce dopants into the plasma state from which smooth solid films are grown. A fast ionization gauge has been used to precisely characterize the feedstock injection phase of each pulse. Diagnostics used to characterize these plasma-polymerized films include profilometry, AFM, SEM, and FTIR.

FF3.16

ENCAPSULATED CHARGED HYDROGELS FOR ELECTRO-MECHANICAL ACTUATION. Patrick T. Mather, University of Connecticut, Storrs, CT; Patrick J. Hood, Cornerstone Research Group, Dayton, OH.

Based on needs of the Air Force and NASA for deployable, active, large aperture optical elements, we have undertaken the development of encapsulated hydrogel actuators. While curvature actuation using hydrated polymers in various forms has been reported, we seek to develop polymer-based actuators with spatially-resolved curvature. Such actuators should enable, for example, actuation of films with more than one curvature axis. Toward these goals, we have synthesized copolymer hydrogel networks based on sodium acrylate, hydroxyethyl acrylate, and methylenebisacrylamide. Rheological, swelling, and thermal characterization have been pursued for hydrogels of varying chemical constitution. Selected hydrogel samples have been processed into encapsulated multilayers for electro-mechanical characterization and testing. The results of material and electromechanical characterization will be reported. In light of our observations, we will provide suggestions for implementation of encapsulated hydrogel actuators in spatially-resolved configurations.

FF3.17

HYPERBRANCHED CONDUCTIVE POLYMERS CONSTITUTED OF TRIPHENYLAMINE. Susumu Tanaka, Kazuhiko Takeuchi, Michihiko Asai, Natl. Inst. of Mat. and Chem. Res., Tsukuba, JAPAN; Tomoaki Iso, Ibaraki Pref. Industry and Tech. Center, Yuhki, JAPAN; Mitsuru Ueda, Tokyo Inst. of Tech., Tokyo, JAPAN.

A hyperbranched conjugated polymer containing triphenylamine was prepared via the coupling of N,N-bis(4-bromophenyl)-N-(4-bromomagnesiophenyl)amine 2. Grignard reagent 2 reacted as an AB₂-type monomer to give hyperbranched conjugated polymer 3 in a one step process. Polymer 3 was also obtained via the Pd-catalyzed coupling of N,N-bis(4-bromophenyl)-4-aminobenzeneboronic acid 4. Polymer 3 had an average molecular weight of 4000-6300 and was found to be soluble in organic solvents such as THF and chloroform, which implies that the hyperbranched polymer 3 is processable. A cast film deposited on a platinum plate was used for cyclic voltammetry. The film showed an anodic peak at 0.95-1.20 V vs. Ag wire. It was dark blue above the oxidation potential and brown-yellow in the neutral state. Polymer 3 was an insulator without doping. When it was doped with iodine, its conductivity rose to 0.8-3.0 S/cm.

FF3.18

POLYACETYLENE-POLYPYRROL ELEMENT. Eugen P. Kovalichuk, Jaroslav S. Kovalyshyn, Lesya S. Kovalyshyn, Chemistry Department, Liviv State University, UKRAINE; M. Stanley Whittingham, Peter Y. Zavalij, Chemistry Department and Material Research Center, SUNY at Binghamton, NY; Ihor Yu. Zavalij, Physics & Mechanic Institute of National Academie of Science of Ukraine, Liviv, UKRAINE.

The method of simultaneous polymerization of acetylene on graphite cathode and pyrrol on Pt anode by the electrolysis of acetylene saturated solutions in propylencarbonate, which contained 1 M lithium perchlorate, 0.1 M nickel(II) perchlorate and 0.1 M pyrrol, has been proposed. The formation of n-doped polyacetylene sheets on the cathode took place under the current of 216 Coulombs through the electrolyzer. Polyacetylene was identified as cis-isomer structure polymer (72%) with conductivity 0.01 Sm/cm. p-Doped polypyrrol was formed on the anode. This electroactive materials has been used for development of the polyacetylene-polypyrrol Li-element, which showed the good capacity, voltage and resistance characteristics during 10 charge-discharge cycles.

SESSION FF4:

Chairs: Yoseph Bar-Cohen and Vivek Bharti
Tuesday Morning, November 30, 1999
Simmons (M)

8:30 AM *FF4.1

ULTRA-HIGH STRAIN RESPONSE OF ELASTOMERIC POLYMER DIELECTRICS. Roy Kornbluh, Ron Peirine, Jose Joseph, Qibing Pei, Richard Heydt, Seiki Chiba, SRI International, Menlo Park, CA.

The deformation of dielectric elastomers under the influence of electric fields has been investigated as a means for actuation. The key design feature of devices based on these materials is the use of highly compliant electrodes that allow the polymer films to expand or contract in the in-plane directions in response to applied electric fields. Many elastomers have been tested and strains over 100% using silicone-rubber elastomers have been measured. The specific elastic strain energy density of such materials is greater than 0.1 J/g. Experimental measurement of the strain vs. applied electric field behavior of several elastomers suggests that the primary electro-mechanical transduction mechanism is due to the electrostatic interaction between free charges on the compliant electrodes. Analysis indicates that the maximum electromechanical coupling efficiency is in the range of 50 to 60%. The large electromechanical response of these materials, as well as other characteristics such as good environmental tolerance and long-term durability, suggest a wide-range of possible applications. Applications that are under active investigation include acoustic actuators for smart skins, microactuators for humps, valves and optics, and artificial muscle actuators for biomorphic robots.

9:00 AM FF4.2

ELECTROSTATIC LAYER-BY-LAYER SELF-ASSEMBLY OF CARBON NANOTUBES. D. Chattopadhyay, K. Ray, A.A.

Zakhidov¹, R.H. Baughman¹ and F. Papadimitrakopoulos*
Department of Chemistry, Polymer Science Program, Nanomaterials Optoelectronics Laboratory, Institute of Materials Science, University of Connecticut, Storrs, CT; ¹Aerospace Technology Group, AlliedSignal Inc., Morristown, NJ.

Electrostatic layer-by-layer self-assembly of oppositely charged molecules and superstructures has proven a convenient method for fabricating conformal multi-layer assemblies. For application in carbon nanotube artificial muscles, our group have extended this methodology to assemble carbon nanotubes with multivalent-metal salts of Nafion, the perfluorinated ion exchange copolymer of tetrafluoroethylene, and perfluoro-[2-(fluorosulfonylhexoxy)propylvinyl ether]. Uniform, micron-thick films of carbon nanotubes and Nafion salts were fabricated using the technique, and characterized by UV-Vis and Raman spectroscopy. The conductivity of these assemblies will be discussed, and related to carbon nanotube percolation in the self-assembled films. The results of impedance spectroscopy based on a quartz crystal microbalance will also be described and used for studying the deposition kinetics and viscoelastic modulus of these assemblies.

9:15 AM FF4.3

NOVEL COMPOSITE ARTIFICIAL MUSCLES (CAM) USING ELECTROACTIVE POLYMERS. Mehran Mojarad, Biomimetic Products, Inc., Albuquerque, NM; David G. Wilson, Waya Research, Inc., Albuquerque, NM.

The office of Naval Research (ONR) has an interest to develop underwater unmanned untethered aquatic vehicles using biomimetic propulsion. Biomimetic Products, Inc. has a research contract to develop biomimetic actuator technology utilizing ion-exchange polymer-metal composite materials. The main focus of this research is to characterize and refine highly efficient material development processes.

The purpose of this research paper is to present the latest development in manufacturing and processing of highly active composite artificial muscles (CAM) using electroactive polymers-metal composites. In addition various actuators made from the CAM film materials for the process of propulsion were characterized and evaluated. A PC-platform bench test setup was made in order to obtain force, speed and other related propulsion parameters for each actuator. Finally the result were compared with some alternative actuators made from other smart materials and discussed advantages and benefits of using the proposed CAM film actuators for the propulsion application.

9:30 AM FF4.4

ELECTROSTRICTIVE GRAFT ELASTOMERS AND APPLICATIONS. Ji Su, National Research Center; Joycelyn S. Harrison and Terry L. St. Clair, NASA-Langley Research Center, Hampton, VA; Yoseph Bar-Cohen and Sean Leary, Jet Propulsion Laboratory/CalTech, Pasadena, CA.

Efficient actuators that are lightweight, high performance and compact are needed to support telerobotic requirements for future NASA missions. In this work, we present a new class of electromechanically active polymers that can potentially be used as actuators to meet many NASA needs. The materials are grafted elastomers that offer high strain under an applied electric field. Due to its higher mechanical modulus, this elastomer also has a higher strain energy density as compared to previously reported electrostrictive polyurethane elastomers. The dielectric, mechanical and electromechanical properties of this new electrostrictive elastomer have been studied as a function of temperature and frequency. Combined with structural analysis using x-ray diffraction and differential scanning calorimeter on the new elastomer, structure-property interrelationship and mechanisms of the electric field induced strain in the grafted elastomer have also been investigated. This electroactive polymer (EAP) has demonstrated high actuation strain and high mechanical energy density. The combination of these properties with its designable molecular composition and excellent processability makes it attractive for applications in actuation tasks. The experimental results will be presented and discussed, and the potential applications in aerospace technology will be reviewed.

10:15 AM *FF4.5

UNIQUE ELECTROPHYSICAL PROPERTIES OF TWO-DIMENSIONAL FERROELECTRIC POLYMER FILMS.

Stephen Ducharme, A.V. Bune, A. Sorokin, University of Nebraska-Lincoln, NE; V.M. Fridkin, S.P. Palto, S.G. Yudin, N. Petukhova, L.M. Blinov, Institute of Crystallography, Russian Academy of Sciences, Moscow, RUSSIA.

Langmuir-Blodgett films of vinylidene fluoride copolymers as thin as 1 nm are the first two-dimensional ferroelectrics. The common ferroelectric properties include the typical first-order ferroelectric-paraelectric phase transition, phase coexistence, hysteresis (switching) and double-hysteresis, the critical point, and finite-size scaling. The films also reveal many unique properties, such as a new surface phase transition, a new bulk phase transition, 1000:1 conductance switching, and the first measurement of the intrinsic coercive field. The Langmuir-Blodgett films have several appealing practical properties, including: piezoelectric response for electromechanical transduction, pyroelectric response for broadband imaging, and polarization bistability for nonvolatile data storage.

10:45 AM FF4.6

STRUCTURAL AND ELECTRONIC CHARACTERIZATION OF EPITAXIALLY-GROWN FERROELECTRIC VINYLIDENE FLUORIDE OLIGOMER THIN FILMS. Kenji Ishida, Kei Noda, Toshihisa Horiuchi, Hirofumi Yamada, Kazumi Matsushige, Kyoto Univ, Dept of Electronic Science and Engineering, Kyoto, JAPAN; Atsushi Kubono, Kyoto Institute of Technology, Dept of Polymer Science and Engineering, Kyoto, JAPAN.

In order to investigate the nanoscopic structure and electric properties of newly synthesized vinylidene fluoride (VDF) oligomers with large electric dipoles, we prepared their thin films of 5-30nm by vacuum evaporation without pyrolysis of samples, and characterized by atomic force microscope (AFM), energy-dispersive grazing incidence X-ray diffractometer (ED-GIXD), fourier transform infrared spectroscopy (FT-IR). As a result, the structural and orientational behavior of VDF oligomer thin films strongly depended on the kinds of substrate and heat treatment during and after film preparation. In particular, the VDF oligomers epitaxially grew on KCl(001) and KBr(001), aligned their molecular chain along the $\langle 110 \rangle$ direction of substrate surface. The ED-GIXD pattern and FT-IR spectra suggested that the films were similar to polar Form I-type crystals of poly(VDF). While, the thin films evaporated on NaCl, Si and some metal substrates were non-polar Form II-type or mixture of both Form I- and Form II-type crystals with their molecular chain normal to the surface. These facts indicated that crystal field of substrate, based on van der Waals and electrostatic interactions, greatly influenced to ferroelectric phase transition of VDF oligomer. In addition, we will demonstrate the fabricating of the local polarized domains in the epitaxial crystals with ferroelectric phase by applying electric pulses from a conducting AFM probe used as a positionable top-electrode, and discuss the nanoscopic ferroelectric properties of VDF oligomers.

11:00 AM FF4.7

VERY THIN CRYSTALLINE FUNCTIONAL GROUP COPOLYMER POLY(VINYLIDENE FLUORIDE-TRIFLUOROETHYLENE) FILM PATTERNING USING SYNCHROTRON RADIATION. Jaewu Choi, H.M. Manohara, E. Morikawa and P.T. Sprunger, Center for Advanced Microstructures and Devices, Louisiana State University, Baton Rouge, LA; P.A. Dowben, Department of Physics and Astronomy and the Center for Materials Research and Analysis, University of Nebraska-Lincoln, Lincoln, NE;

Crystalline 5 monolayer poly (vinylidene fluoride-trifluoroethylene, P(VDF-TrFE)) copolymer films were studied as a function of a synchrotron radiation exposure using ultraviolet photoemission spectroscopy and mass spectroscopy. Initial exposure of synchrotron X-ray white light ($h\nu < 1000$ eV) onto the P(VDF-TrFE) films, induces substantial chemical bonding configuration from single to double bonding in the chain and formation of the crosslinking in-between chains. As the result, the new valence band features near the Fermi level are proportionally developed with increasing the exposure amount of the white light, and the valence band maxima crosses the Fermi level. The crosslinking in-between polymer chains is proportionally developed with increasing the white light exposure. The photodetached fragments of the copolymer P(VDF-TrFE) are mainly consisted of H_2 , HF, CHF, CH_2 and relatively small amount of photodetached F and CF_2 are observed. The emitting ratio of the photodetached fragments depends on the exposure time. The photodetachable functional group P(VDF-TrFE) films turns out to be a strong candidate for the direct patterning and it is demonstrated here. With the direct patterning of the functional group, the Fermi level crossing with large amount of X-ray irradiation suggests that a direct metallic wiring can be simultaneously conducted.

11:15 AM FF4.8

PVDF AND PZT DETECTORS TO MEASURE THE PULSE ENERGY OF HIGH POWER Ti:SAPPHIRE LASERS. Ting Shan Luk, David E. Bliss, Stewart M. Cameron, Sandia National Laboratories, Albuquerque, NM; Larry Lee, K-Tech, Albuquerque, NM.

We present a novel application of piezo-electric sensors to measure the energy of a high energy density ultra-short pulse laser beam. Pulse energy is arguably the most important parameter to measure but it can also be problematic since the laser intensity is above the ablation threshold of solid materials. Using a pick-off optic to measure a fraction of the laser intensity is not an option either as the optic is damaged also. Our approach is to measure the amplitude of the shock wave generated in a linearly elastic media as a monitor of the energy deposited by the laser beam. PVDF polymer films are ideally suited since they can be fabricated into small volume devices with a high bandwidth response. Devices are calibrated with a laser beam having a known energy and focussed to a tight spot and also with a gas gun. A comparison of the response of ceramic PZT and Polymer PVDF sensors will be presented.

SESSION FF5:

Chairs: Katherine Bohon and Jerry I. Scheinbeim
Tuesday Afternoon, November 30, 1999
Simmons (M)

1:30 PM *FF5.1

NOVEL POLYMER ELECTRETS. Gerhard M. Sessler, Univ of Technology, Dept of Electrical Engineering, Darmstadt, GERMANY.

Polymer electrets are permanently charged insulators which show electroactive behavior due to their external or internal electric fields. Recently, a number of new polymer materials has been developed which exhibit improved electrical and mechanical properties. One such group of substances are the cycloolefin copolymers (COC) consisting of ethylene and the cyclic olefin monomer 2-norbornene. These materials can be made with different compositions having different glass transition temperatures. Amorphous and semicrystalline modifications are available, some containing antiblocking additives. COC polymers are nonpolar and their electret properties are entirely due to real charges. Isothermal and thermally-stimulated measurements on corona-charged COC-films indicate that positively surface-charged samples are excellent electrets in humid and dry atmospheres and at elevated temperatures. Their charge-retention characteristics are comparable to those of the best known polymer electrets, namely the fluorocarbon materials, and they are superior with respect to their mechanical behavior. They may be of interest in electrostatic sensor and actuator applications and as electret air filters. Other new electret materials are cellular polymer films consisting of polypropylene or fluorocarbon with flat air enclosures, occupying about 50 to 70 percent of the volume. Corona charging of these films results in discharges within the air enclosures and thus leads to opposite-polarity charging of opposite surfaces of these voids. Due to these charges and the small Young's modulus, such materials exhibit strong pseudo-piezoelectric behavior. They are thus reversible electromechanical transducers with high transducer constants. Measurements of these constants show the reciprocity of the transducer operation (i.e., the operation as sensor and as actuator with the same transducer constants), which can also be derived from a simple model of the material.

2:00 PM *FF5.2

NON-ELECTRICAL POLING IN NOVEL FERROELECTRIC POLYMERS. S. Tasaka, Department of Materials Science and Technology, Faculty of Engineering, Shizuoka University, Hamamatsu, JAPAN.

Non-electrical poling in novel ferroelectric amorphous polymers including polythioureas, polycyanophenylenesulfides, and polyvinylfluorides was investigated. This poling method utilizing the cooperativity of molecular dipoles can be called "surface energy poling" and takes advantage of the energy difference in the top and bottom surface of a polar aggregate (dipole glass) to form a remanent polarization. These ferroelectric polymer films sandwiched between a metal with higher surface energy and PTFE film with lower surface energy was heated to $T_{cp}=T_{gx}1.2$ and cooled slowly to room temperature. In the thin films less than $10\mu m$, we observed the remanent polarization which gives large pyroelectric and piezoelectric constants as well as that obtained by electrical poling. This poling cannot be realized for inhomogeneous structures such as crystalline ferroelectric VDF polymers.

2:30 PM FF5.3

POLARIZATION STABILITY OF AMORPHOUS PIEZOELECTRIC POLYIMIDES. Cheol Park¹, Zoubeida Ounaies², Ji Su¹, Joseph G. Smith Jr. and Joycelyn S. Harrison, Advanced Materials and Processing Branch, NASA/Langley Research Center, Hampton VA; ¹National Research Council, ²ICASE.

Amorphous polyimides containing polar functional groups such as nitrile dipoles have been synthesized and evaluated at NASA/LaRC for use as high temperature piezoelectric sensors. Most of previous studies have focused on fully cured polymers. In this study, we investigated poling of partially cured polymers and its effect on the remanent polarization (P_r) and the piezoelectric strain coefficient (d_{31}). We also evaluated the thermal stability of these polymers as a function of various curing and poling conditions under dynamic and static thermal stimuli. In the first case, the polymer samples were thermally cycled under strain by systematically increasing the maximum temperature from $50^\circ C$ to $200^\circ C$ and measuring the d_{31} coefficient. In the second case, the samples were annealed at an elevated temperature, and then isothermal decay of the P_r was measured at room temperature as a function of time. Both conventional and corona poling methods were used for comparison. Corona poling was used in an attempt to maximize degree of dipolar orientation and minimize localized arcing during imidization. The aligned polar groups could be immobilized by additional imidization of these partially cured polymers and then a subsequent cooling while the applied field was being applied.

2:45 PM FF5.4

RESPONSIVE SIDE CHAIN LIQUID CRYSTALLINE POLYURETHANES. Bindu R. Nair, Vasilis Gregoriou and Paula T. Hammond, Department of Chemical Engineering, MIT, Cambridge, MA.

Side chain liquid crystalline segmented polyurethanes with MDI or HDI hard segments and nematic or ferroelectric mesogens pendant on polysiloxane soft segments have recently been synthesized. These unique materials have been engineered to couple the responses of liquid crystals and thermoplastic elastomers to produce mechanooptically active materials. The design, synthesis and characterization of this new class of materials will be presented. The effect of varying the molecular structure of various parts of the macromolecule on the physical properties and microphase segregation behavior of the polyurethanes will be discussed. Some general observations on the interplay between polyurethane morphology and liquid crystalline phases will be offered. Finally, static and dynamic FT-IR dichroism data will be used to develop a mechanical deformation model for these new materials so that the effects of the hard segments on the liquid crystalline alignment with applied strain can be elucidated.

3:00 PM FF5.5

A STUDY OF LIQUID CRYSTALLINE ELASTOMERS AS PIEZOELECTRIC DEVICES. Andrew G. Biggs, Keith M. Blackwood, Stuart Dailey, DERA Malvern, Malvern, Worcestershire, UNITED KINGDOM; Adrian Bowles, DERA Farnborough, Farnborough, Hampshire, UNITED KINGDOM; Alison May, Merck UK Ltd, Southampton, UNITED KINGDOM.

A study of the work carried out by DERA over the past three years into the synthesis and development of novel ferroelectric liquid crystalline elastomers is presented. Along with the results of a study on their potential application as piezoelectric devices for novel and improved acoustic sensor materials. Some model compounds have shown piezoelectric activity over ten times that of PVDF and current

systems show levels of activity approaching those of PVDF and co-polymers. The model low molar mass systems have given d_{33} coefficients in the range of 200 pC/N. The development of these model systems into stable elastomeric configurations with low T_g and reasonable sensitivity is described. Future developments and possible applications are then described.

3:15 PM **FF5.6**

DIPOLAR RELAXATION DYNAMICS IN SIDE-CHAIN ELECTROACTIVE COPOLYMERS FUNCTIONALIZED WITH THE AZO DYE DISPERSE RED13. Paulo António Ribeiro, Universidade Nova de Lisboa, Faculdade de Ciências e Tecnologia, Departamento de Física, Monte Caparica, PORTUGAL; Débora Tereza Balogh, José Alberto Giacometti, Universidade de Sao Paulo Instituto de Física de Sao Carlos, Sao Carlos, SP, BRAZIL.

The orientational relaxation process in a side-chain methacrylate copolymer functionalized with the dipolar azo chromophore 4-[N-ethyl-N-(2-hydroxyethyl)]-amino-2-chloro-4-nitroazobenzene, DR13, was investigated. The decay of the orientational order was monitored by electrooptical measurements in samples poled by corona discharge near the glass transition temperature and by optical poling at room temperature. The isothermal decay of the electrooptic coefficient r_{13} was successfully fitted with both the Kohlrausch-Williams-Watts stretched exponential equation and the power law equations of the Dissado-Hill many body model. Both these formalisms offer a microscopic explanation of the relaxation processes which will be discussed. The effect of the thermal treatment on the relaxation was also investigated prior and during the poling process. A considerable increase in the relaxation KWW characteristic time constant occurred when the samples were cooled at a very low rate during the poling process. This was to be expected from the decrease in the free volume upon thermal treatment.

SESSION FF6:

Chairs: Yoseph Bar-Cohen and Gerald H. Pollack
Wednesday Morning, December 1, 1999
Simmons (M)

8:30 AM ***FF6.1**

POLY(SNS) ELECTROCHEMICAL SYNTHESIS AND PROCESSABILITY. T.F. Otero, S. Villanueva, Laboratorio de Electroquímica, Universidad del País Vasco, San Sebastian, SPAIN; E. Brillas, Departament de Química Física; J. Carrasco, Departament d'Enginyeria Química i Metallúrgia, Facultat de Química, Universitat de Barcelona, Barcelona, SPAIN.

Conducting polymers are considered in literature as one of the most important components of organic metals. Many of the studied conducting polymers seem to lack some of the most specific polymeric properties: solubility and fusibility. The interest in our laboratories was centered in a main question: if conducting polymers reproduce most of the electrochemical properties of inorganic metals, like oxidation and reduction processes, it could be possible to generate a polymer able to mimic electro-dissolution and electrodeposition process. Those processes are the origin of many industrial processes: electroerosion, electromachining, electroforming, electroplating, electrophotography, electrolitography, etc. In order to produce polymers able to be electrochemically solved, our aim was to find conducting polymers, which oxidized and reduced states show different solubilities. In this way the method of synthesis of 2,5-di(-2-thienyl) pyrrole, SNS, was improved. The electrochemical oxidation of monomer from LiClO₄ acetonitrile solutions gives a film of poly-conjugated and lineal oxidized chains, which solve in most of the organic solvents. The kinetics of the electro-synthesis of this polyconjugated material was followed by ex situ ultramicrogravimetry. The electrochemical reduction of the film in aqueous solution gives an insoluble film of the reduced material. On this way both, oxidized and reduced states of the material, are available as solid films. The flow of an anodic current through a solution of reduced material gives a faradaic electrodeposition of the oxidized state. The process was also followed by microgravimetric determination of the deposited dry films. Checking different electrolyte productivities similar to those obtained during electro-dissolution were obtained. The resulting films were also soluble in organic solvents. The influence of the different chemical and electrical variables in both electro-dissolution and electrodeposition processes were studied. Acknowledgments: This work was supported by the M.E.C. of the Spanish Government.

9:00 AM **FF6.2**

POLYMER MICROMUSCLES. Edwin W.H. Jager, Olle Inganäs, Applied Physics Dept., Linköping University, Linköping, SWEDEN.

Bilayers of passive conductors and conjugated polymers can be used as actuators. In the electrochemically driven transformation of the polymer from a neutral semiconductor to a metallic phase, there is

accompanying volume change. Such actuators work in aqueous electrolytes, and are therefore suitable for biological environments. We study microactuators based on such bilayers, and develop tools for biomedical studies. Patterning of thin polymer and conductor layers down to 10 μm lateral dimensions is used to prepare microrobots actuated by applications of potential. We demonstrate microrobotic hands, extending out from the surface and capable of gripping and holding small objects.

9:15 AM **FF6.3**

CONDUCTION BEHAVIOR OF DOPED POLYANILINE UNDER HIGH CURRENT DENSITY AND THE PERFORMANCE OF AN ALL POLYMER ELECTROMECHANICAL SYSTEM. Haisheng Xu, Z.-Y. Cheng, Q.M. Zhang, Materials Research Laboratory, The Pennsylvania State University, University Park, PA; Pen-Cheng Wang, Alan MacDiarmid, Chemistry Department, University of Pennsylvania, Philadelphia, PA.

In many device applications, such as electro-acoustic transducers and actuators based on high strain electroactive polymers, there are many advantages to utilize conductive polymers as electrodes. However, in these applications, a high electric power usually is required which translates to high voltage and high current in the system. Hence, the maximum current density which a conducting polymer can carry is of great interest and importance. In this paper, the conduction behavior at high current density of polyaniline(PANI) films doped with HCl and camphor sulfonic acid (HCSA), respectively, is reported. It was found that the current density deviates strongly from the ohmic relation with the electric field in high current density region and a saturation of the current density was observed. The maximum current density J_m observed is proportional to the conductivity of the samples and for PANI doped with HCSA, J_m can reach as high as 1200 A/cm². Making use of the conducting polymer as the electrodes for the electrostrictive P(VDF-TrFE) copolymer, an all-polymer electromechanical system was fabricated. The all-polymer films exhibit similar or larger electric field induced strain responses than those from films with gold electrodes, presumably due to reduced mechanical clamping from the electrodes. In addition, the all-polymer system also exhibits comparable dielectric and polarization properties to those of gold-electroded P(VDF-TrFE) films in a wide temperature (from -50°C to 120°C) and frequency range (from 1Hz to 1MHz). These results demonstrate that conducting polymers can be used for many electro-acoustic devices and provide improved performance. This work was supported by the Office of Naval Research by Grant No: N00014-98-1-0254.

9:30 AM **FF6.4**

COMPARATIVE STUDY OF THE SOLVENT EFFECT ON THE ELECTROCHEMICAL DEPOSITION OF POLYTHIOPHENE AND POLYBITHIOPHENE. T.K.S. Wong, Photonics Laboratory, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore, SINGAPORE; X. Hu, Polymer Laboratory, School of Applied Science and Advanced Materials Research Centre, Nanyang Technological University, Singapore, SINGAPORE.

Electrically conducting polymers (ECPs) is one of the three main classes of electroactive polymers. ECPs are usually prepared by chemical synthesis or electrochemical polymerization. Although the latter technique can yield a film directly and allow reversible doping/dedoping, control of the microstructure and quality of the deposited film is usually not straightforward. This is because the various deposition variables: applied bias, monomer, solvent and electrode surface etc. are interrelated. The organic solvent used in particular has a profound effect on the deposited layer. The purpose of this study is to conduct a systematic investigation into the effect of the organic solvent on the electrochemical deposition of polythiophene (Pth) and polybithiophene (PBth). The polythiophenes were chosen because of their important applications in organic field effect transistors (OFETs). For each monomer (thiophene and bithiophene), electrochemical polymerization was carried out using acetonitrile and benzonitrile as solvent. Other deposition conditions were kept constant. Pth and PBth films with different thickness were deposited onto indium tin oxide (ITO) glass. The change of surface morphology with deposition time was observed using ex-situ tapping mode atomic force microscopy (TMAFM) and optical microscopy. Topographic images of films at an early stage of deposition from the two solvents will be presented and compared. For acetonitrile, continuous films of Pth and PBth consisting of nanometre size granules were seen in all depositions. For benzonitrile, the initial polymer deposit (especially for Pth) consists of small discrete islands rendering the film discontinuous. An explanation of the observations based on the different nucleophilicities of the solvents and supported by mechanical strength measurements will be given.

10:15 AM **FF6.5**

EQCM AND QUARTZ CRYSTAL IMPEDANCE MEASUREMENTS FOR THE CHARACTERIZATION OF THIOPHENE-BASED

CONDUCTING POLYMERS. Catia Arbizzani, Francesca Soavi, Bologna Univ, Dept of Chemistry "G. Ciamician", Bologna, ITALY; Marina Mastragostino, Palermo Univ, Dept of Physical Chemistry, Palermo, ITALY.

EQCM was extensively used to investigate ion-transport phenomena during doping-undoping processes for electronically conducting polymers. Several early studies assumed that the polymer films were rigidly coupled with the crystal so as to apply the Sauerbray equation. However, the rigidity of electronically conducting polymer films is doubtful and it has to be demonstrated. Crystal impedance analysis is of paramount importance to get insight into the viscoelastic properties of the film and to avoid misleading in the interpretation of EQCM data. This contribution will present EQCM and crystal impedance data collected during electropolymerization and during doping/undoping processes of thiophene-derivative electronically conducting polymers and the results will be analyzed and discussed referring to the model proposed for viscoelastic films [1]. [1] H.L. Bandey, A.R. Hillman, M.J. Brown and S.J. Martin, *Faraday Discuss.* 107 (1997) 105-121

10:30 AM FF6.6

POLYTHIOPHENE GRAFTED ON POLYETHYLENE SURFACES. N. Chanunpanich, A. Ulman, Polytechnic Univ, Dept. of Chemical Engineering, Chemistry and Material Science and the NSF MRSEC for Polymers at Engineered Interfaces, Brooklyn, NY; Y.M. Strzhemechny, S.A. Schwarz, Queens College of CUNY, Flushing, NY; A. Janke, H.G. Braun, T. Kratzmueller, Inst for Polymer Research, Dresden, GERMANY.

Polythiophene was grafted onto PE film by three chemical reaction steps: a bromination of PE film, a substitution reaction with 2-mercaptothiophene sodium salt, and a chemical oxidative polymerization with thiophene. The PE films were brominated in the gas phase at room temperature, yielding PE-Br films. XPS results showed the appearance of bromine peak at binding energy of 70 eV, with a Br/C ratio of 0.8 %. AFM topography showed that the roughness (Ra value) of the film increased from 2.7 nm (pristine) to 3.1 nm after bromination. Substitution reaction of PE-Br film with 2-mercaptothiophene sodium salt was carried out in DMF/Ethanol, yielding a reddish PE-S-T film. XPS results showed a S/C ratio of 0.6 %. Further more, ATR-FTIR indicated that 2-mercaptothiophene was introduced on the PE film. Chemical oxidative polymerization of PE-S-T with thiophene was carried out in a suspension solution of FeCl₃-3 and dry CHCl₃-3, yielding PE-PT film. Scanning electron micrograph revealed the island of polythiophene (PT) on the PE film. XPS results indicated the increasing of sulfur intensity. ATR-FTIR supported that polymerization mainly took place at 2,5 position. Doping with 0.1% FeCl₃ in acetonitrile gave a green film. After exposing to ethanol, the color of the film changed back to a reddish film. Conductivity measurements are reported.

10:45 AM FF6.7

A NEW CONDUCTIVE COMPOSITE FILMS BY PERMEATION METHOD. Wang Jinwei, M.P. Srinivasan, Department of Chemical & Environmental Engineering, National University of Singapore, SINGAPORE.

A new method of making conductive composite films by permeation of the conducting guest species into the host is reported. A layer of poly(3-n-dodecyl thiophene) is embedded at the surface of polyimide by permeation of the monomer or polymer (in solution in tetrahydrofuran or chloroform) into a solution of polyamic acid in n-methyl pyrrolidinone or dimethyl acetamide. The resulting composites were imidized and polymerized (if monomer is used to make the conductive layer). Chemical imidisation yielded composite films that retained the conducting polymer even after solvent extraction. The films were conductive upon doping with iodine and recovered conductivity when they were exposed to iodine vapor subsequent to thermal de-doping. Thermogravimetry showed that the amount of thiophene incorporated into the polyimide was higher for permeation of the polymer than of the monomer; however, the latter was still higher than the amount that could be incorporated by blending. The levels of conductivity and speed of recovery for doped films were also higher for the permeated films. Results of scanning electron microscopy suggested that the higher mobility afforded by contact in the liquid state may have contributed to greater entanglement between the constituents leading to higher thermal and solvent resistance of the conducting constituent. The permeation method could be easily adapted to form composite films in solvent systems that not completely miscible.

11:00 AM FF6.8

ELECTROCHEMICAL INVESTIGATION OF 2,2'-DIAMINO-BENZYLOXYDISULFIDE. Yuzhi Su, Kecheng Gong, South China University of Technology, Polymer Structure & Modification Research Lab, Guangzhou, CHINA.

A new conducting polymer, poly(2,2'-diaminobenzoyloxydisulfide (DABO)), has been proposed as a positive material suitable for secondary lithium batteries^[1-2]. With the aim of better understanding the process of polymerization and depolymerization of 2,2'-diaminobenzoyloxydisulfide(DABO). The redox behavior, kinetic reversibility and adsorption of DABO have been investigated at platinum electrode in acetonitrile solution by using linear sweep voltammetry, the cyclic sweep voltammetry and the rotating disk electrode technique. These experiments clearly showed the reaction is chemically reversible but kinetically slow at ambient temperature and charge transfer is the rate-determining step, but chemical dimerization is at equilibrium. The results are common to many organic disulfides. Furthermore, the striking observation from cyclic voltammograms is the smaller separation of the anodic and cathodic peak owing to the specific structure of DABO, compared with other organic disulfides. This result indicates the redox reaction of DABO is higher kinetically reversible and poly(DABO) positive material is expected to deliver higher power output or energy efficiency.

Reference:

1. Yuzhi Su, Wwnshi Ma, Kecheng Gong, Abstract of 1999 MRS Sping Meeting, CC7.5, San Francisco (1999.4)
2. Kecheng Gong, Wenshi Aa, Mat. Res. symp. Proc., 411, 351(1995)

11:15 AM FF6.9

ON THE NATURE OF HETEROGENEITY IN VACUUM DEPOSITED POLYANILINE FILMS. V.F. Ivanov, O.L. Gribkova, A.A. Nekrasov, and A.V. Vannikov, Frumkin Institute of Electrochemistry, Moscow, RUSSIA.

Heterogeneity of polyaniline and other conductive polymers in intermediate oxidation states is fundamental problem of physics and chemistry of these ones. Usually only advanced methods may be used for immediate detection of the heterogeneity in the molecular scale range. For the first time we have observed the process of the heterogeneous net-like structure formation in macroscopic scale under the oxidation of the evaporated polyaniline films by aqueous HNO₃ and other oxidative agents. Formation of heterogeneous dissipative structure is explained in terms of nonequilibrium thermodynamic and chemical kinetics. The study was supported by International Science and Technology Center (project 872) and Russian Foundation for Basic Research (grants No. 99-03-32077 and No. 96-15-97320).

SESSION FF7:

Chairs: Takeo Furukawa and Qiming Zhang
Wednesday Afternoon, December 1, 1999
Simmons (M)

1:30 PM *FF7.1

MUSCLE CONTRACTION AS A POLYMER-GEL PHASE-TRANSITION. Gerald H. Pollack, Univ of Washington, Dept of Bioengineering, Seattle, WA.

I present evidence that the mechanism of muscle contraction is fundamentally similar to the mechanism of contraction of many artificial muscles. Artificial muscles typically contract by a polymer-gel phase-transition. Upon transition, the polymer does work, shortens and develops tension. Real muscle is thought to operate differently. The textbook view is that contraction occurs by a sliding-filament mechanism. One set of constant-length filaments is presumed driven past another by the action of cyclically rotating cross-bridges much like the rowing of a boat. However, cross-bridge rotation has proved resistant to confirmation. Further, there is mounting evidence that the filaments do not remain at constant length; they appear to shorten when activated. These features seem inconsistent with the textbook mechanism. In considering alternatives, it is natural to think of a phase-transition. Shortening of protein filaments is analogous to the collapse of polymers during a phase-transition, and the biological event occurs in a critical, all-or-none fashion much like the polymeric event. Further, contraction can be triggered by the same array of stimuli that trigger ordinary polymer-gel phase transitions, including change of pH, increase of salt concentration, temperature change—even electrical stimulus. Thus, the principles of natural muscle contraction may be useful in establishing optimal design principles for artificial muscles.

2:00 PM FF7.2

BIOCHEMICAL SYNTHESIS AND UNUSUAL CONFORMATIONAL SWITCHING OF MOLECULAR COMPLEX OF POLYANILINE AND DNA. Ramaswamy Nagarajan, Sukant K. Tripathy, Department of Chemistry, Center for Advanced Materials, University of Massachusetts Lowell, Lowell, MA; Lynne A. Samuelson, Ferdinando F. Bruno, U.S. Army Soldier & Biological Chemical Command, Natick Systems Center, Natick, MA.

Polyaniline (PANI) is one of the extensively investigated conducting polymers because of its promising electrical properties and unique redox tunability. Recently a new template assisted, enzymatic synthetic approach has been developed which yields a water-soluble and conducting complex of polyaniline and the template used. The conditions of this approach are extremely mild and allow for the utilization of more delicate biological systems as template materials, such as DNA. Here we report the extension of this enzymatic approach to DNA by first investigating the use of poly (vinyl phosphonic acid) as a precursor template to demonstrate feasibility. DNA also serves as a suitable template for complexation and formation of conducting polyaniline. Circular dichroism results suggest that the secondary structure of the DNA may be reversibly switched through manipulation of the redox state of the polyaniline. These studies suggest exciting new possibilities in the use of this complex for the fabrication of nano-wires, biosensors, diagnostic tools and for unique fundamental studies to "probe" the structure and function of DNA. The detailed characterization and discussion of these studies will be presented.

2:15 PM FF7.3

ELECTROCHEMICAL DEPOSITION OF CONDUCTING POLYMERS ON NEURAL PROSTHETIC DEVICES. Xinyan Cui, David C. Martin, Univ of Michigan, Dept of Material Science and Engineering, Macromolecular Science and Engineering Center, Ann Arbor, MI; David J. Anderson, Univ of Michigan, Dept of Electrical Engineering and Computer Science, Ann Arbor, MI.

Micromachined neural prosthetic devices facilitate the functional stimulation of and recording from the peripheral and central nervous systems. However, they suffer from certain problems including the loss of electrical activity as a function of time and the migration of the device from the intended site of implantation. The deposition of bioactive, electrically conductive polymer coatings onto the surfaces of neural prostheses has been proposed as a possible solution to these problems. Polypyrrole was precisely deposited onto the functional sites of neural prosthetic probes by potentiostatic and galvanostatic electropolymerization from aqueous solution, using 0.1 M sodium salt of poly(styrene sulfonate) as dopant. The influence of current density, monomer concentration, and reaction time on the thickness and morphology of the polypyrrole films has been studied by Optical Microscopy, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The electrical properties of the film were studied by Impedance Spectroscopy (IS) and Cyclic Voltammetry (CV). The impedance of the film varied with film thickness and roughness. An optimum thickness exists in terms of the lowest impedance at the biologically-relevant frequency of 1 kHz. The roughness of the film is being studied, quantified and related to the charge transfer capability of the film. In-vivo acute recording tests in guinea pig cortex showed that strong neural signals can be detected with the polypyrrole-coated probes.

2:30 PM FF7.4

ENZYMATIC TEMPLATE SYNTHESIS OF POLYPHENOL. Ferdinando F. Bruno, Lynne Samuelson, Materials Science Team, Natick Soldier Center, U.S. Army Soldier, Biological, Chemical Command, Natick, MA; Ramaswamy Nagarajan, Sukant Tripathy, Department of Chemistry, Center for Advanced Materials, University of Massachusetts Lowell, Lowell, MA; Sidhartha S. Jena, Ke Yang, Jayant Kumar, Department of Physics, Center for Advanced Materials, University of Massachusetts Lowell, Lowell, MA .

Phenolic polymers are of great interest for a number of electronic and industrial applications. Unfortunately, the toxic nature of the starting materials (formaldehyde) and extreme reaction conditions required for the synthesis of these polymers has severely limited their use in today's markets. We present here an alternative, biocatalytic approach where the enzyme horseradish peroxidase (HRP) is used to polymerize phenol in the presence of an ionic template. Here the template serves as a surfactant type of matrix that can both emulsify the phenol and polyphenol chains during polymerization and maintain water solubility of the final polyphenol/template complex. The reactants and conditions of this approach are extremely mild and result in high molecular weight, electronically active and water-soluble complexes of polyphenol with the template used. Polystyrene sulfonate, lignin sulfonate and dodecyl benzene sulfonate (micelles) were the templates investigated in this study. In each case, soluble polyphenol complexes were formed with molecular weights ranging in the millions. Thermal analysis and UV-Vis spectroscopy shows that these complexes have exceptional thermal stability and a high degree of backbone conjugation. Conductivities on the order of 10^{-5} S/cm are observed. In the case of the SPS template, a polyphenolic gel complex is formed which may then be dialyzed, vacuum dried and redissolved in water/DMSO. This enzymatic approach offers exciting opportunities in the synthesis and functionalization of a new class of processable polyphenolic materials. The detailed characterization and discussion of these studies will be presented.

3:15 PM FF7.5

MULTILAYER GELS FOR ELECTRICALLY DRIVEN LINEAR ACTUATORS. Paul Calvert and Zengshe Liu, University of Arizona, Tucson, AZ.

Acidic polymer hydrogels, such as cross-linked polyacrylic acid, have long been explored for use as muscle-like actuators. They originally had the disadvantages of being too weak, too slow of working only underwater and of responding to an applied electrical potential only by bending. Each of these problems can be addressed a functioning muscle does not yet exist. We have developed layered structures combining active acidic gels with passive neutral gels in order to produce a material that changes shape but not volume when a potential is applied. This system can show a linear expansion and contraction of 10% with an applied potential of $\pm 6V$ for 1 minute in each direction. This paper will discuss the role of electrode reactions in this process and efforts to miniaturize this material.

3:30 PM FF7.6

CONSTITUTIVE RESPONSE OF ACTIVE POLYMER GELS. Steven P. Marra, K.T. Ramesh and A.S. Douglas, Johns Hopkins University, Dept. of Mechanical Engineering, Baltimore, MD.

Ionic polymer gels can achieve large, reversible deformations in response to environmental stimuli, such as the application of an electric field or a change in pH level. Consequently, great interest exists in using these gels as actuators and artificial muscles. The goal of this work is to develop a means of characterizing the mechanical properties of ionic polymer gels and to describe how these properties evolve as the gel actuates. A biaxial testing system has been developed which can measure stresses and deformations of thin gel films in a variety of liquid environments. Experimental results on polyacrylonitrile gels have shown these films to be nonlinearly viscoelastic and capable of large recoverable deformations in both acidic and basic environments. The mechanical properties of this gel are shown to evolve as the gel actuates. Preliminary results on constitutive modeling of the coupled behavior will also be presented.

3:45 PM FF7.7

BENDING OF SULFONATED HYDROGELS IN DC ELECTRIC FIELDS. Li Yao, Sonja Krause, Rensselaer Polytechnic Institute, Department of Chemistry, Troy, NY.

A reversible bending occurs when a partially sulfonated (50% sulfonation) triblock copolymer of styrene-*b*-ethylene-*co*-butylene-*b*-styrene (S-SEBS) is placed between electrodes in a DC electric field of 2.5 V/cm in aqueous solutions. The S-SEBS gel strip responds to the electric field immediately and reaches a steady bending state in less than 20 seconds. However, the life-time of the S-SEBS gel in the experiments is limited by the lack of chemical crosslinks in the network. Therefore, a series of crosslinked S-SEBS gels were prepared by gamma irradiation. The bending behavior of the crosslinked gels in electrolyte solutions with various cation sizes including Na^+ , Cs^+ , $(CH_3)_4N^+$, and $(C_4H_9)_4N^+$ showed qualitative similarities between chemically crosslinked and physically crosslinked gels but there were quantitative differences. The quantitative differences indicate a difference in morphology between chemically and physically crosslinked gels. Comments about the mechanism of the bending is going to be discussed. This work is supported by ONR and NSF (Grant No. DMR-952126).

4:00 PM FF7.8

ELECTROACTIVE NONIONIC POLYMER GEL - SWIFT BENDING AND CRAWLING MOTION - Toshihiro Hirai, Jian-Ming Zheng, Masashi Watanabe, Shigeyuki Kobayashi, Shinshu Univ, Faculty of Textile Sci and Technol, Nagano, JAPAN; Mitsuhiro Hirai, Gunma Univ, Faculty of Eng, Maebashi, JAPAN.

Nonionic polymer gel swollen with dielectric solvent could be actuated by an electric field. As a typical example, poly(vinyl alcohol) gel swollen with dimethyl sulfoxide was investigated. The gel sheet could be bent over 90 degree in 60 ms, when the field was applied through thin gold electrodes on the gel surfaces. The gel showed crawling motion when it was placed on electrodes arrayed on a glass plate. The worm-like crawling of ca.1cm was completed in one sec. The gel is homogeneous and the strain is proportional to the square of the electric field. These phenomena were explained by a novel concept of charge injected-solvent-drag. The concept will be shown to be applicable to some other polymers, suggesting that many conventional polymer gel materials can be used as electroactive actuator.

4:15 PM FF7.9

EFFECT OF THE PORE FORMATION ON THE SOLUTION FLOW THROUGH ACRYLAMIDE GELS. Hirohisa Tamagawa, Suzana Popovic, Minoru Taya, Univ. of Washington, Dept. of Mechanical Engineering, Seattle, WA.

Pore formation in gel is supposed to be a promising way to realize the fast volume change of gel. A simple synthesis method of porous gels is proposed. Tiny pores were formed in acrylamide gel quite homogeneously. The pore formation is dominated by the amount of polymerization initiator (ammonium persulfate), polymerization accelerator (N,N,N',N'-tetramethylethylenediamine) used and the pregel solution stirring speed in the course of gel synthesis. The size of pores can be controlled by these factors to some extent. This pore formation method was applied to the other type of polymer gels conventionally synthesized by radical polymerization. They were also made to be porous structured quite successfully. The investigation on the flow of iodine solution through the non-porous and porous acrylamide gels was conducted under the different temperature, 10, 20, 30 and 40°C. From this experiment, it was found that the diffusion distance, x , follows a standard one-dimensional diffusion equation, $x = \sqrt{2Dt}$, where D and t are a diffusion coefficient and time, respectively. It was also found that D of porous gel was larger than that of non-porous gel. Therefore by the pore formation in gel, it is possible to improve the gel volume change speed to some extent. This is supposed to be due to the shortening of diffusion path by pores created in gel. But still the solution movement seems to be largely restricted even in the highly porous gel network. To sum up, it is necessary to reduce the size of gel to realize further fast volume change.

4:30 PM FF7.10

THE ELECTROMECHANICAL RESPONSE OF POLY-DIMETHYLSILOXANE NETWORKS CONTAINING ELECTORRHEOLOGICAL FLUIDS. Katherine Bohon, Sonja Krause, Rensselaer Polytechnic Institute, Dept of Chemistry, Troy, NY.

An electrorheological fluid (ERF) was made using polyaniline (PANI) particles suspended in a trimethyl terminated polydimethylsiloxane (3MPDMS) fluid. This ERF was then cured into matrices of both ordered and randomly crosslinked PDMS networks (XPDMS). Electric fields were applied to these systems using both rigid and flexible electrodes. Both electrode displacement and compression modulus of many of the composite gels were measured as a function of crosslink density of the gels, viscosity of the 3MPDMS fluid, conductivity and dielectric constant of both the pure PANI particles and the gel matrix, weight percent PANI in the ERF, volume percent ERF in the final gel composite, and applied electric field. The DC electric field required for a single electrode displacement of 50 micrometers using an ordered XPDMS matrix was approximately half that needed when a randomly crosslinked gel of comparable crosslink density was used. When the ERF particles were pre-aligned in a XPDMS network, the force generated by the actuator was increased. Decreasing the viscosity of the ERF phase increased the electrode displacement observed under comparable conditions. In order to obtain electrode displacements in less than 0.1 second, all components of the composite gels were necessary.