

SYMPOSIUM EE

Electroactive Polymers and Their Applications as Actuators, Sensors, and Artificial Muscles

November 26 – 27, 2001

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* Invited paper

8:30 AM *EE1.1

CONDUCTING POLYMERS AND CARBON NANOTUBES AS ELECTROMECHANICAL ACTUATORS AND STRAIN SENSORS. Geoffrey M. Spinks, Gordon G. Wallace, Lu Liu, Dezhi Zhou, University of Wollongong, Intelligent Polymer Research Institute, Wollongong, AUSTRALIA.

Electromechanical actuators are being investigated for a wide range of applications in medical, electronics and industrial areas. There is a wide range of electromechanical actuator materials but both conducting polymers and carbon nanotubes are attractive because of their low voltage operation. For practical applications, the strain generated by the actuator must be known under different applied loads. Unfortunately, there is very little information about the performance of polymer actuators at different loads: most studies report the strain generated at zero, or near zero, loads. We have measured the isotonic strain for both polypyrrole films and carbon nanotube sheets at increasing applied loads and found a linear decrease in strain with increasing stress. The rate of strain decrease with increasing stress was far greater for the polypyrrole actuator than for the carbon nanotube sheets. Analysis of the deformation induced during electrochemical charging and discharging of the materials shows that a decrease in strain with increasing load can be attributed to a change in the elastic modulus of the material during charging (doping). Thus, the polypyrrole modulus changes significantly between the oxidized (high modulus) and reduced (low modulus) states. The difference in modulus can be as much as 100% for these materials which correlates with the rapid decrease in actuator strain with increasing applied stress. Another aspect of the practical use of actuator materials is their control. We have developed simple strain sensors based on conducting polymer - coated stretch fabrics. Calibration of these materials shows a wide linear range and high gauge factor (~ 2). Combining fabric strain gauges with polymer actuators is a convenient means for providing feedback control to the actuating element.

9:00 AM EE1.2

EFFECT OF FABRICATION ON MORPHOLOGY AND ACTUATION OF SINGLE WALL CARBON NANOTUBE/NAFION COMPOSITES. Debjit Chattopadhyay, Izabela Galeska, Fotios Papadimitrakopoulos, Nanomaterials Optoelectronics Laboratory, Department of Chemistry, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT; Ray Baughman, Honeywell Co., Morristown, NJ.

Recently 'bucky' papers fabricated from single wall carbon nanotubes (SWNTs) were shown to possess significant promise as non-faradaic electrochemical actuators based on their high electrical conductivity and excellent mechanical properties. However, morphological and physical effects, including nanotube bundling, have resulted in poor mechanical properties and low electrochemically generated strains. Herein we demonstrate that processing SWNTs with polymeric electrolyte (Nafion[™]) and alternative fabrication strategies hold significant promise for enhanced actuator performance. The annealed SWNTs/Nafion composites have higher densities (up to 0.75 g/cm^3), larger surface areas (c.a. $500 \text{ m}^2/\text{g}$), superior actuation strains (0.4% in 1 M NaCl) and more uniform morphologies when compared to pure 'bucky' papers. Moreover the X-ray diffraction along the edge of the SWNTs/Nafion annealed composite showed partial anisotropy as opposed to totally isotropic pure bucky papers.

9:15 AM *EE1.3

ELECTROMECHANICAL EFFECTS IN FERROELECTRIC LIQUID CRYSTALLINE ELASTOMERS. Friedrich Kremer, Walter Lehmann, University of Leipzig, Faculty of Physics and Geosciences, Leipzig, GERMANY; Elisabeth Gebhard, Rudolf Zentel, University of Mainz, Institute of Organic Chemistry, Mainz, GERMANY.

Michelson-Interferometry is employed to study electromechanical effects in selfsupporting homeotropically oriented layers of ferroelectric liquid crystalline elastomers (FLCE) (1,2). Applying electrical fields in the direction parallel to the smectic layers results in strong thickness charge perpendicular to the layers. The measured inverse electrostrictive (response in the second harmonic) effects by two order of magnitude the data measured for conventional "smart" ceramics (3,4). The molecular origin of this giant electrostrictive response is based on the electroclinic effect, which is well known for low molecular weight systems.

1. W. Lehmann, L. Hartmann, F. Kremer, P. Stein, H. Finkelmann, H. Kruth, S. Diele J Appl Phys 86: 1647 (1999).
2. F. Kremer, H. Skupin, W. Lehmann, L. Hartmann, P. Stein, H.

Finkelmann Adv in Liquid Crystals 113: 183 (2000).

3. W. Lehmann, H. Skupin, F. Kremer, E. Gebhard, R. Zentel Ferroelectrics 243: 107 (2000).

4. W. Lehmann, H. Skupin, C. Tolksdorf, E. Gebhard, R. Zentel, P. Krueger, M. Loesche, F. Kremer Nature 410: 447 (2001).

9:45 AM EE1.4

SOFT ACTUATORS BASED ON ELECTROCHEMOMECHANICAL EXPANSION AND CONTRACTION IN CONDUCTING POLYMERS, POLY(3-ALKYLTHIOPHENE) FILMS.

Masaki Fuchiwaki, Osaka Technology and Science Center, Osaka, JAPAN; Wataru Takashima, Keiichi Kaneto, Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, Fukuoka, JAPAN.

Upon oxidization, conducting polymers swell as well as increase in the conductivity. The change of dimension upon electrochemical cycle is called electrochemomechanical deformation (ECMD), which can be utilized as soft actuators. There has been a great number of studies on ECMD in conducting polymers like polyaniline (PAN), polypyrrole (PPy) and their derivatives. The mechanisms of ECMD have been revealed to be due to (1) insertion and exclusion of bulky ions, (2) conformation change of structure by the delocalization of π -electrons and (3) electrostatic repulsion between like charges. It has been shown that actuators based on conducting polymers generate greater force than that of gel and ion exchange resins. However, the quantitative measurements for various conducting polymers have not been carried out sufficiently. In this report, quantitative studies of ECMD behaviors in head-tail poly(3-alkylthiophene) (HT-PAT) with alkyl = hexyl (PAT6), alkyl = dodecyl (PAT12) and non-regiocontrolled (NR)-PAT6 and NR-PAT12 are described. The ECMD of the PAT films was measured in nonaqueous electrolyte solution of tetrabutylammonia furuoroborate with respect to the electrochemical expansion and contraction and their cycle response. The results are discussed taking the morphology of film, comparing with ECMD behaviors of polyaniline (PAN), poly(o-methoxyaniline) (PmAn) and polypyrroles (PPS) films. As a result, the expansion/contraction ratio of PAT films is ranging 2~3%, which is comparable to those of PAN and PmAn films. The expansion and contraction ratio is larger in PAT6 films compared with that of PAT12 films, because of the higher density of π -conjugation in PAT6 films. Large creeping effect was observed in NR-PAT films, contrary to the case of HT-PAT films.

10:30 AM EE1.5

MONOLITHIC CONDUCTING POLYMER ACTUATORS BASED ON ASYMMETRICALLY CONFIGURED POLYANILINE MEMBRANES. Hsing-Lin Wang, Bioscience Division, B-4, Los Alamos National Laboratory, Los Alamos, NM.

We report synthesis and characterization of polyaniline integrally skinned asymmetric membranes (PANI ISAMs), and the use of these membranes to fabricate conducting polymer actuators. PANI ISAMs prepared from highly concentrated PANI solution comprised of a thin dense skin and a microporous substructure, and a density gradient throughout the cross section from the dense skin side to the porous side. Expansion coefficient of the doped PANI ISAMs is density dependent, where the dense skin side expand more as compare to that of the porous side. With optimized experimental conditions, bending angles of greater than 180 degree is achieved in less than a second. We have also fabricated membranes with mechanical strength approaching the thermally cured dense film (2.3 GPa). PANI ISAM monolithic actuator was fabricated. Detailed study on their performance and underlying mechanism as electrochemical actuators will also be discussed.

Funding provided by NASA and DOE is greatly appreciated.

10:45 AM EE1.6

A NEW CONCEPT FOR ACTUATORS BASED ON CONDUCTING INTERPENETRATING POLYMER NETWORKS. Frederic Vidal, Hyacinthe Randriamahazaka, Claude Chevrot and Dominique Teyssie, LPME, University of Cergy-Pontoise, FRANCE.

Conducting polymers could provide actuator materials that work in a similar manner to natural muscles. Recent proposals increasingly report combinations of electronic conducting polymers arranged in a bilayer type geometry and sandwiching a solid electrolyte. One of the weak points in these bilayer type actuators is the interface and the adhesion between the conducting polymers and the solid electrolyte on the one hand and the long term stability of the air exposed conducting polymer. In this work, a different approach is proposed in order to solve both problems. IPN type materials are synthesized between poly(3,4-ethylenedioxythiophene) and a combination of an ionic conducting polymer network (polyethyleneoxide based) and various thermoplastics. The synthetic pathway which will be presented ensures a gradual dispersion of the electronic conducting polymer through the thickness of the network i.e. the concentration decreases from the outside towards the center of the film. The system

is thus similar to a layered one with the advantage that the conducting polymer is protected from the environment and the intimate combination of the three polymers needs no adhesive interface. The influence of the morphology and chemical composition of the matrix on the electrochemical characterization of the material have been studied. The best results are obtained for about 80% polyethyleneoxide in the matrix where the material remains elastomeric enough and still keeps good mechanical properties due to the polycarbonate partner. Moreover the addition of plasticizing oligomers which increase the free volume improves the surface conductivity which can reach 15 S/cm. A study of the influence of the nature of the electrolytes on the intensity of the current shows that KClO₄ gives better results than LiClO₄. Finally, we showed that this electrochemical actuator is capable of a 45 degree angular deflexion under a 0.5 V potential difference.

11:00 AM EE1.7

PARALLEL ELECTROCHEMICAL METHODS TO ACCELERATE ELECTROACTIVE MATERIAL DISCOVERY AND OPTIMIZATION. Peter G. Madden, John D. Madden, Ian W. Hunter, Massachusetts Institute of Technology, Cambridge, MA.

In the search for new electroactive polymer materials, determining which materials are most promising and finding optimal synthesis conditions can be difficult and time consuming. There is a need for parallel synthesis and experimentation techniques that can accelerate the discovery process. We have developed an eight cell parallel electrochemical synthesis and testing platform. The system bandwidth of over 10 kHz is well above the maximum 1 kHz frequencies that are of interest for characterizing our conducting polymer actuators. A peak current of 100 mA provided by each of the eight cell potentiostats is ample for the small working electrode sizes used (~10⁻⁶ m²). Typical synthesis for polypyrrole shows film growth rates on the order of 1-10 nm/s at current densities around 0.1 to 1.0 A/m² and can be done at temperatures down to -50°C. Initial results are presented that use linear system identification techniques to measure the electrochemical impulse and frequency response of polypyrrole synthesized under different conditions.

11:15 AM *EE1.8

EAP BASED SKIN AND MUSCLES FOR MAN MACHINE INTERFACES. Daniilo De Rossi, Alberto Mazzoldi, Centro "E. Piaggio", Faculty of Engineering, University of Pisa, Pisa, ITALY.

Biomimetic EAP sensors and actuators are being developed in forms which enable distributed skin-like and pseudomuscular systems. Conducting electrostrictive and piezoresistive polymers in form of fibers, threads and fabrics have been made and their mechanoelectric transduction properties quantified. Wearable haptic interface in form of a sensory-motor glove has been designed under solid biomechanical arguments and then built. It is intended to be used in the virtual reality and rehabilitation fields. An android face has also been constructed, endowed with stereotypical expressivity. Facial movements are governed by biomimetic actuators and controlled by learning algorithm and a limited set of actor face expression. Animatronics is its intended field of use. This talk will mostly address crucial material issues to be identified and solved to realize truly effective interfaces.

SESSION EE2: ELECTROACTIVE POLYMER DEVICE APPLICATIONS (INCLUDING THIN FILMS)

Chairs: Siegfried Bauer and Qiming Zhang
Monday Afternoon, November 26, 2001
Fairfax (Sheraton)

1:30 PM EE2.1

THE ELECTROACTIVE POLYMERS INFRASTRUCTURE. Yoseph Bar-Cohen, JPL, Pasadena, CA.

In the last ten years, new EAP materials have emerged that exhibit large displacement in response to electrical stimulation enabling great potential for the field. To develop efficient EAP that are robust for practical applications there is a need to establish an adequate EAP infrastructure. This requires developing adequate understanding of EAP materials' behavior, as well as effective processing and characterization techniques. Enhancement of the actuation force requires understanding the basic principles using computational chemistry models, comprehensive material science, electro-mechanics analytical tools and improved material processing techniques. Efforts are needed to gain better understanding of the parameters that control the EAP electro-activation force and deformation. The processes of synthesizing, fabricating, electroding, shaping and handling need to be refined to maximize the EAP materials actuation capability and robustness. Methods of reliably characterizing the response of these materials are required to establish database with documented material properties in order to support design engineers

considering use of these materials and towards making EAP as actuators of choice. Various configurations of EAP actuators and sensors need to be studied and modeled to produce an arsenal of effective smart EAP driven system. The development of the infrastructure is a multidisciplinary task involving materials science, chemistry, electro-mechanics, computers, electronics, and others. This paper will be a review of the status of the EAP infrastructure and the challenges to practical application of EAP materials as actuators.

1:45 PM *EE2.2

SOUND REFLECTION AND ABSORPTION BY PIEZOELECTRIC POLYMER FILMS. Hidekazu Kodama, Munehiro Date, Eiichi Fukada, Kobayasi Institute of Physical Research and Rion Co., Ltd., Dept. of Research and Development, Tokyo, JAPAN; Tomonato Okubo, Kobayasi Institute of Physical Research, Tokyo, JAPAN.

It has been found that the elastic properties of piezoelectric materials are controlled by connecting negative capacitance circuits. The stress-induced charge is amplified by the circuit and the feedback voltage is applied on the materials. The direct and inverse piezoelectric effects are thus superposed. By matching the capacity and resistance of the circuits to those of piezoelectric materials, the apparent elastic constants of the materials are arbitrarily increased or decreased depending on the kind of the circuit. The present paper describes experiments on sound reflection and absorption using this principle. About 10 μm thick films of PVDF or P(VDF/TrFE) were installed in the center of an acoustic tube with a 43 μm diameter and about 1 m length. Glass wool or urethane foam was placed behind the film to keep this under tension. Using a standard two-microphone method the absorption coefficient and transmission loss of the film were determined as a function of frequency. With the circuit increasing the elastic constant, 10-20 dB increase of transmission loss (increase of reflection) was observed at arbitrary tuned frequencies. With the circuit decreasing the elastic constant, the increase of the absorption coefficient was observed at tuned frequencies. By choosing appropriate circuit components, 10 dB sound isolation over a frequency range from 200-1200 Hz was achieved. A piezoelectric ceramic PZT plate was fixed between a shaker and a mass and connected to a negative capacitance circuit. The transmissibility of vibration through the PZT plate was determined as a function of frequency. When the circuit components were adjusted to match with the impedance of PZT plate, the sharp decrease of transmissibility by 60 dB was observed at 3kHz. Owing to the high piezoelectric activity in PZT, the complete isolation of vibration was achieved. New applications of piezoelectric polymers and ceramics in noise control and vibration suppression are proposed.

2:15 PM *EE2.3

FERROELECTRIC POLYMERS FOR HIGH PRESSURE AND SHOCK COMPRESSION SENSORS. Francois Bauer, Institut Franco-Allemand de Recherches de Saint-Louis, ISL, Saint-Louis, FRANCE.

Ferroelectric polymers (PVDF) with well-defined and precisely known electrical properties are now routinely available from commercial sources. Electrical processing with the Bauer poling method can produce individual films with well-defined remanent polarization up to 9 μC/cm². These polymers provide an unusual opportunity to study the structure and physical properties of materials subjected to shock loading. The behaviour of PVDF has been studied over a wide range of pressures using high-pressure shock loading and has yielded well-behaved reproducible data up to 25 GPa in inert materials. The application of PVDF gauges for recording shock waves induced in polar materials like polymers or in reactive materials is hampered by observations of anomalous responses due to shock-induced polarization. A solution using an appropriate electrical shielding has been identified and applied to PVDF for shock measurements of polymer (Kel-F), and for Hugoniot measurements of High Explosives (H.E.). Furthermore, shock pressure profiles obtained with in situ PVDF gauges in porous H.E. in a detonation regime have been achieved. Typical results of shock pressure profile versus time show a fast superpressure of a few nanoseconds followed by a pressure release down to a plateau level and then by a pressure decay. These observations have raised the question of the loading path dependence of the piezoelectric response of PVDF at high shock pressure levels. Consequently, studies of the piezoelectric behavior of PVDF gauges under impact loading using a two-stage light gas gun have been conducted. Results show that the PVDF response appears independent of the loading path up to 30 GPa. P(VDF-TrFE) copolymers exhibit unique piezoelectric properties over a wide range of temperature depending on the composition. Their properties and phase transition are being investigated. These copolymers are also strong candidates for electroactive applications. Emphasis of the presentation will be on key results and implications.

2:45 PM EE2.4

DEVICE FABRICATION AND PERFORMANCE OF

ELECTROSTRICTIVE P(VDF-TrFE) BASED ACTUATORS AND TRANSDUCERS. Z.-Y. Cheng, T.-B. Xu, R.W. Cui, J. Hundal and Q.M. Zhang, Materials Research Laboratory, The Pennsylvania State University, University Park, PA; W.C. Chen, Mechanical Engineering Department, The Pennsylvania State University, University Park, PA.

The large electrostrictive strain and high elastic energy density make the newly developed electrostrictive P(VDF-TrFE) copolymers very attractive for a broad range of actuator and transducer applications. More importantly, it is found that the electromechanical coupling factor for the stretched electrostrictive P(VDF-TrFE) copolymer can reach more than 45%. In order to explore the application of the advanced properties observed in this material in practice devices, we investigated a few prototype actuator and transducer devices made use of the stretched electrostrictive copolymer. The results from two kinds of the devices, flexensional transducers and MEMS-type unimorph actuators, are presented to demonstrate the high electromechanical output of the devices. In the flexensional transducer, a multilayer stack of 1 mm thickness and 1 inch square size, made of thin films of the electrostrictive P(VDF-TrFE) copolymer, was fabricated and characterized first. Both the static and resonance results indicate that the multilayer stack performance is very close to what expected of parallel layer actuator. A flexensional transducer was formed by attaching bow shaped metal sheets to the two sides of the multilayer stack. The performance of the transducer was characterized in air and under water. The test results show that this new type of flexensional transducer can generate giant displacement, several mm, at non-resonance condition. The resonance frequency is about a few kHz depending on the device size. The performance of the MEMS is characterized in both air and liquid medium. For a typical device with 1 mm length, the displacement at the middle point reaches more than 70 mm and the ratio of the displacement/applied voltage is more than 180 nm/Vrms at non-resonance condition. More importantly, over more than 3 frequency decades (up to 100 kHz), the dispersion of the displacement is less than 20%.

3:30 PM *EE2.5

ELECTROSTRICTIVE ELASTOMERS AND APPLICATIONS IN AEROSPACE TECHNOLOGIES AND MISSIONS. Ji Su and Joycelyn S. Harrison, Advanced Materials and Processing Branch, NASA Langley Research Center, Hampton, VA.

Recent development of electroactive polymers has offered us several new candidates: electrostrictive copolymer, electrostatic elastomers, electrostrictive liquid elastomers and electrostrictive graft elastomers. These polymers have exhibited very promising electromechanical properties in one way or another, such as large electric field induced strain, and/or high strain energy density, for many applications. However, understanding mechanisms for the electromechanical functionality of these polymers and utilizing the knowledge of the understanding to develop better electroactive polymers are still challenges. This presentation will discuss the mechanisms of non-liquid crystal electrostrictive elastomers, such as electrostrictive polyurethane and electrostrictive graft elastomers. These will include primary contributions to the electric field induced strain and secondary effects on the performance of the materials. Based on the understanding of the mechanisms, the route of molecular engineering to develop new electromechanically functional polymers will also be discussed. In addition to the discussion on the materials, applications of the materials in aerospace technologies and some NASA missions will be presented.

4:00 PM *EE2.6

THICKNESS DEPENDENCE OF FERROELECTRIC PROPERTIES IN COPOLYMERS OF VINYLIDENE FLUORIDE AND TRIFLUOROETHYLENE. Takeo Furukawa, Shigeru Sakai and Yoshiyuki Takahashi, Science University of Tokyo, Faculty of Science, Tokyo, JAPAN.

Ferroelectric properties in random copolymers of vinylidene fluoride and trifluoroethylene were investigated with special interest on their thickness dependence. Thick film samples (10 μ m-1mm) prepared by solvent casting followed by uniaxial-drawing and annealing had extremely well oriented and highly crystalline structures and exhibited typical ferroelectric polarization reversal and Curie transition behavior as well as large piezoelectric and pyroelectric activities. A spin-coating technique was employed to prepare very thin film samples (10nm-1 μ m). As the thickness was decreased below 100nm, ferroelectricity became obscure to disappear completely at 10nm. The ferroelectric switching time became markedly longer and the dielectric relaxation strength associated with cooperative dipolar motion diminished with decreasing thickness. Combining the results of dielectric, X-ray, IR and AFM measurements, we shall discuss about the factors governing loss of ferroelectricity in ultra thin VDF/TrFE films.

4:30 PM EE2.7

FINITE SIZE EFFECT IN FERROELECTRIC POLYMER THIN AND ULTRATHIN SPIN CAST FILMS. Feng Xia, H.S. Xu, B. Razavi, Z.-Y. Cheng, and Q.M. Zhang, Penn State University, Materials Research Laboratory, University Park, PA.

Ferroelectric polymer thin films have gained a lot of attention due to their emerging applications in MEMS, memory devices, and pyroelectric sensors. Thin ferroelectric polymer films also provide unique system to investigate the finite size, dimensional, and interface effects in the ferroelectric materials. Recently, we examined the structures, morphology, and ferroelectric switching behavior in spin cast P(VDF-TrFE) thin and ultrathin films (from 40 nm to 1 mm) on electroded silicone wafer. It was observed that the ferroelectric behavior in these films does not change with thickness and the observed changes in various properties are caused by interface effects and also by the change of the crystallinity. However, the activation energy increases as the film thickness is reduced, this phenomenon is caused by the interface effect, most likely due to the charge injection process across metal-polymer film interface barrier. Furthermore, for films below 100 nm, there is an additional large increase of the activation energy with reduced film thickness, which is caused by the precipitous drop of the film crystallinity (as verified by the X-ray and AFM data) at that thickness. The result indicates that for the spin cast P(VDF-TrFE) thin films, there exists a critical thickness, below which the crystallization process is strongly hindered. Detailed X-ray study on films annealed under different conditions suggests that this critical thickness in the crystallization process of polymer thin films is determined by the crystallite lamella width along the film thickness direction.

4:45 PM EE2.8

MORPHOLOGY, MELTING, AND RECRYSTALLIZATION OF FERROELECTRIC LANGMUIR-BLODGETT FILMS OF P(VDF-TRFE) COPOLYMERS. M. Bai, Matt Poulson, A.V. Sorokin, Stephen Ducharme, Department of Physics and Astronomy and Center for Materials Research and Analysis, University of Nebraska, Lincoln, NE; V.M. Fridkin, Institute of Crystallography, Russian Academy of Sciences, Moscow, RUSSIA.

We report the investigation of the morphology of films of vinylidene fluoride (70% mol) and trifluoroethylene (30% mol) copolymer made by Langmuir-Blodgett (LB) deposition on Si (100) wafers and annealed at 120°C. X-ray diffraction and infrared ellipsometry measurements show that the films are highly planar with the ferroelectric β phase structure having (110) orientation, where the polymer chains are parallel to the film and the CF₂-CH₂ dipoles are tilted from the film normal. Melting the film at 150°C and then slowly cooling it results in destruction of the (110) crystallites and growth of needle-like structures with dimensions approximately 6 μ m long by 0.3 μ m wide, resembling lamellae lying on the substrate, as observed by scanning electron microscopy. The melted films have polymer chain segments tilted out of the film plane, as confirmed by infrared ellipsometry.

This work is supported by National Science Foundation and by the Nebraska Research Initiative.

**SESSION EE3: POSTER SESSION
NOVEL ELECTROACTIVE POLYMERS I**

Chair: Qiming Zhang
Monday Evening, November 26, 2001
8:00 PM
Exhibition Hall D (Hynes)

EE3.1

CHARACTERIZATION OF ORDERED MESOPOROUS CONDUCTING POLYMER FILMS. Yun-Ju Lee, Katharine A. Pfenning, Stephanie A. Pruzinsky, Paul V. Braun, UIUC, Dept of Mat Science and Eng, Urbana, IL.

It has been demonstrated that colloidal crystals formed by self-assembly from colloidal suspensions can template the synthesis of various materials, leading to mesoporous solids with translationally ordered pores following the removal of the colloidal crystal template. Here, we demonstrate the electrochemical synthesis of thin films of mesoporous poly(pyrrole) on glassy carbon, showing complete infilling of interstitial voids by the conducting polymer and successful removal of the contiguous colloidal crystal template. Such mesoporous conducting polymer films are promising due to the close contact between the film and the supporting electrolyte, which may speed up or alter the relatively slow counter ion mass transport kinetics that in many cases represent the rate-limiting factor in the charging and discharging of conducting polymers. We present the results of electrochemical characterization of mesoporous poly(pyrrole) films. Cyclic voltammetry and chronoamperometry indicate that mesoporous

conducting polymer films operate under different kinetics compared with bulk films. It is hypothesized that such difference originates in part from the availability of small reservoirs of counter ions and electrolytes present in the interconnected pores. Understanding the kinetics may enable the fabrication of devices such as supercapacitors and fast-response actuators from conducting polymers.

EE3.2

SENSING MECHANISM OF CONDUCTING POLYMER SENSOR FOR VOLATILE ORGANIC COMPOUNDS. Jeung-Soo Huh, Ha Ryong Hwang, Jin Gyu Roh, Duk Dong Lee, Environmental Gas Monitoring Lab, Kyungpook National University, Taegu, KOREA; Jeong-Ok Lim, Medical Research Institute, Kyungpook National University, KOREA.

The importance of environment gas monitoring is well understood and much research has focused on the development of suitable gas sensitive materials. Among many different types of gas sensors, metal oxide and conducting polymer type sensors are most popular. There has recently been interest in the use of conducting polymers such as polypyrrole (PPy) and polyaniline (PANi) as sensors for volatile organic compounds (VOC). PPy and PANi detect VOCs at room temperature and their synthesis method is simple. Sensing principle associated with conducting polymers is in progress. However little is explained on the mechanism of conducting polymer sensing on gas molecules, especially VOCs. In this study, we fabricated chemically polymerized PPy and PANi films with different selectivity by controlling doping time. The sensing properties and mechanism of VOCs adsorption to conducting polymers were investigated with contact angle measurements, scanning probe microscope and UV-vis spectrophotometer. Upon gas adsorption, polypyrrole exhibited positive sensitivity while polyaniline had negative sensitivity. PPy film shows hydrophilic property and PANi film shows hydrophobic property. After gas adsorption, the sensitivity increases as a function of the polarity of adsorbed molecules. We found that conducting polymer sensor is very sensitive to the difference in polarity of gas molecules.

EE3.3

THIACROWNETHER INCORPORATED METHACRYLATE POLYMERS FOR MERCURY ION SENSORS FOR MICROSENSOR SOLUTION. Jagannathan Arockiam, Thomas Johnson, Valiyaveetil Suresh, Lee Hian Kee, National University of Singapore, SINGAPORE.

Due to the high demand for smart sensors in environmental monitoring and biomedical applications, major studies are underway towards the development of sophisticated sensors with real-time applications. The major roadblock in developing a chemical sensor lies in the modification of the functional layer. We have explored the possibility of developing metal ion sensors using crownether as a sensing moiety. We incorporated the thiocrownether by covalent bond to a methacrylate polymer backbone. From the extraction studies, the polymer is found to be an excellent candidate for the mercury sensor applications. This paper will focus on the synthesis, metal extraction studies and the fabrication of the sensor.

EE3.4

AN ENHANCED REDOX PROCESS OF CYTOCHROME C DISULFIDE AT POLYANILINE FILM ELECTRODE. Yanxiu Zhou, Bin Yu, Kalle Levon, Dept. of Chemistry and Chemical Engineering, Brooklyn, NY.

Conducting polymer, polyaniline, was used as a probe to analyze the role of cytochrome c disulfide in the redox transition of cytochrome c. Peak potential separation of 122 mV between the cathodic and anodic peak with a formal potential of 0.308 V (vs. NHE) of disulfide presenting in cytochrome c became 70 mV on a polyaniline electrode. This enhancing effect can be attributed to the formation of adducts between the disulfide group and the N sites in the polyaniline moieties. As a result, the presence of disulfides in cytochrome c was responsible for the lack of electrochemical response of the hemin group on the electrodes, such as gold, platinum electrode, which have high affinities towards adsorption of sulfur-containing protein. The mechanism for the effect was studied using electrochemistry and Raman spectroscopy.

EE3.5

SURFACE MODIFICATION OF NEURAL RECORDING MICROELECTRODES BY CONDUCTING POLYMERS. Xinyan Cui, David C. Martin, University of Michigan, Macromolecular Science and Engineering Center, Ann Arbor, MI.

Micromachined multichannel neural probe consists of silicon shanks that have gold or iridium microelectrode sites on their surface. They have been successfully used in acute neural recording from central nervous system, but their recording capability degrades after a few weeks of implantation. Clearly, improvement of the electrode-tissue interface needs to be done to enhance signal transport and chronic

stability. Conducting polymer polypyrrole and poly(3,4-ethylenedioxythiophene) (PEDOT) have been deposited on the electrode sites electrochemically. The deposited conducting polymer film provides an interface with much higher surface area and lower impedance than the metal electrode sites. CDPGYIGSR is a fragment of laminin and has been proved to be able to promote neuron attachment. Decipeptide DCDPGYIGSR was synthesized and co-deposited with polypyrrole or PEDOT onto the neural electrodes. In cell culture test, conducting polymer/peptide coated electrode attracted local attachment of neurons, which demonstrated the bioactivity of the peptide in the polymer films. The peptide in the conducting polymer coating was proved to be stable by microfocusing infrared spectroscopy after 3 months of soak testing in de-ionized water. The electrochemical property of the conducting polymer was examined by cyclic voltammetry. PEDOT was a more robust material than polypyrrole under electrochemical cycling. Chronic implantation of polypyrrole / peptide coated probes was performed and followed by neural recording. After 2 weeks, the probe was explanted and examined for neuron attachment. It was found that neurons preferentially attached onto the peptide coated electrode site and stable single unit of neural activity was recorded through those sites.

EE3.6

FERROELECTRIC PROPERTIES OF VINYLIDENE FLUORIDE OLIGOMER. Kenji Ishida^{1,2}, Kei Noda¹, Atsushi Kubono³, Toshihisa Horiuchi¹, Hirofumi Yamada¹ and Kazumi Matsushige¹. ¹Kyoto Univ, Dept of Electronic Science and Engineering, Kyoto, JAPAN. ²PREST-JST. ³Kyoto Institute of Technology, Dept of Polymer Science and Engineering, Kyoto, JAPAN.

Ferroelectric polymers are attractive for various application fields, such as sensor, actuator and molecular ferroelectric devices. However, it is difficult to clearly discuss the polarization mechanism in molecular scale on the polymers due to the wide distribution of molecular weight and the coexistence of crystal and amorphous regions. Therefore, we selected a newly synthesized vinylidene fluoride (VDF) oligomer, $\text{CF}_3(\text{CH}_2\text{CF}_2)_{17}\text{F}$, with low molecular weight and its narrow distribution, and studied on structure and local piezoelectric behavior of VDF oligomer thin films. Here, we report their ferroelectric properties investigated by polarization response. VDF oligomer thin films of 5-100 nm were prepared by vacuum evaporation without pyrolysis. The structures of VDF oligomer thin films strongly depended on the kinds of substrate and heat treatment during and after film preparation. In particular, the VDF oligomer films with ferroelectric crystal phase could be prepared on metal substrate at low substrate temperature. Then, the top electrode was evaporated on the film for the electric measurement. The polarization hysteresis loops and I-V characteristics were evaluated by direct charge/current measurement system using high S/N op-amp. The difference of ferroelectric properties between polymer and oligomer films as well as dependency on their crystal phases will be discussed.

EE3.7

FERROELECTRIC POLARIZATION REVERSAL OF POLYMERS UNDER HIGH HYDROSTATIC PRESSURE. Susumu Ikeda, Toshinao Yuki, Takeshi Nojiri, Hideshige Suzuki, Tomonori Koda, Yamagata Univ, Dept of Polymer Science and Engineering, Yonezawa, JAPAN.

Polymers which exhibit ferroelectric properties are classified into three stages. Some fluoro-polymers give clear polarization reversal phenomena and sharp ferroelectric-paraelectric phase transitions. Some polymers including urethane and urea groups have the possibility of ferroelectricity but the polarization reversal phenomena characteristic of ferroelectric materials have not been confirmed so far. On the other hand, odd-number nylons including odd carbons in a monomer exhibit a clear polarization reversal process although they do not give any phase transition below the melting temperature. In this paper, we report on their ferroelectric polarization reversal under high hydrostatic pressures. Specifically, we compare the ferroelectric polarization reversal of nylon 11 with those of copolymers of vinylidene fluoride (VDF) and trifluoroethylene (TrFE). The hydrostatic pressure affects directly interchain interaction. Since the polarization reversal occurs due to the rotation of a molecular chain around the chain axis in both cases of nylon 11 and VDF-TrFE copolymers, the effect of the hydrostatic pressure upon the polarization reversal phenomena reflects the nature of the intermolecular interaction controlling the ferroelectric properties of these polymers. So we discuss the physical nature of the polarization reversal phenomena of these ferroelectric polymers.

EE3.8

HIGH FREQUENCY DIELECTRIC RELAXATION IN POLYMERS FILLED WITH FERROELECTRIC CERAMICS. Natsuko Noda and Jan Obrzut, National Institute of Standards and Technology, Gaithersburg, MD.

We have investigated high frequency relaxations in polymer composite films filled with ferroelectric ceramics. Such materials can be used in the construction of embedded passive devices in microwave circuits and fast digital electronics. In order to extend the dielectric measurements to the microwave range, we developed an accurate measurement technique that utilizes a thin film capacitance terminating a coaxial waveguide. The complex permittivity measured at frequencies of 100 Hz to 10 GHz for several films 50 μm to 100 μm thick, having the dielectric constant of 2 to 30, was fitted to a dielectric model as a superposition of Havriliak-Negami functions. An intrinsic high frequency relaxation process has been identified in the polymers filled with ferroelectric ceramics. It was found that the position of the loss peak depends on the relaxation of the polymer matrix, while its magnitude is amplified by the permittivity of the ferroelectric component. Thus, both the values of the dielectric constant as well as the position and magnitude of the loss peak can be controlled by modifying the composition of the dielectric material at the molecular level.

SESSION EE4: NOVEL ELECTROACTIVE
POLYMERS II

Chairs: Yoseph Bar-Cohen and Eiichi Fukada
Tuesday Morning, November 27, 2001
Fairfax (Sheraton)

8:30 AM *EE4.1

TOWARD MOLECULAR MUSCLES: DESIGN OF SINGLE MOLECULE ELECTROMECHANICAL ACTUATORS BASED ON POLY(TETRA[2,3-THIENYLENE])S. Michael J. Marsella, University of California, Department of Chemistry, Riverside, CA.

Electrically conducting polymers (CPs) have the ability to function as bulk electromechanical actuators (EMAs), and have been utilized in the fabrication of microactuator devices. The interest in further shrinking devices to the molecular level has intensified in recent years, including the concept of a molecular actuator (molecular muscle). In the case of traditional (bulk) CP-EMAs, actuation results from volume changes occurring in the bulk material via redox-induced counterion intercalation (expansion) and expulsion (contraction). In contrast, poly(tetra[2,3]thienylene) has been specifically designed to function as a single molecule EMA. In this system, the tetra[2,3]thienylene repeat unit serves as a masked [8]annulene, and expansion and contraction of the polymer chain results from a redox-induced conformational change that occurs at each tetra[2,3]thienylene repeat unit. Specifically, the conformational change that affords single molecule EMA is analogous to the tub-to-planar interconversion that is observed in the reversible reduction of cyclooctatetraene. Definitive evidence of single-molecule EMA in poly(tetra[2,3-thienylene]) has been elusive, as analysis is complicated by the fact that traditional methods of determining EMA in bulk systems do not apply to analysis at the single molecule level. These issues, as well as progress to date in the pursuit of a functional "molecular muscle" will be reported.

9:00 AM *EE4.2

GIANT ROTARY POWER AND LIGHT MODULATION BY POLYLACTIC ACID FILM. Yoshiro Tajitsu, Yamagata Univ, Dept of Polymer Sci & Engr, Yonezawa, Yamagata, JAPAN.

Aliphatic polyester is an example of such polymers; in particular, expectations for polylactic acid (PLA) in which molecules containing asymmetric carbon atoms have a helical orientation have been expected, for a long time, to exhibit optical activity with significantly higher optical rotary power in their solid state, compared with inorganic low-molecular-weight crystals. We examined the optical rotation and light modulation properties of poly-L-lactic acid (PLLA) and poly-D-lactic acid (PDLA) films in which the higher-order structure is controlled by forging. The findings from this study are summarized as follows:

1) Existence of significant rotatory power in the fiber axis direction of PLLA and PDLA films.

PLLA and PDLA films possess levorotatory power and dextrorotatory power, respectively. The optical rotatory power of a PLLA film is 3200 degrees/mm and approximately 100 times greater than that of quartz. The required thickness of a component is 10 mm for a PLLA film, while it is 1 mm for quartz.

2) Demonstration of light modulation by PLLA films.

We confirmed light modulation up to 10 MHz. Since the PLLA film provides a fast response, we believe that a light modulation speed in the GHz range using a more modified PLLA sample is possible.

Acknowledgments:

This work was supported in part by Grants-in-Aid of Scientific Research (No. 13650944) from the Ministry of Education, Science, Sports and Culture, Japan.

We would like to thank Dr. Y. Shikinami of Takiron Co., Ltd for providing us with PLA samples.

9:30 AM EE4.3

FORCE, TIME RESPONSE AND EFFICIENCY OF IONIC METAL POLYMER COMPOSITES. Anthony Kucernak, Department of Chemistry, Imperial College of Science, Technology and Medicine, London, UNITED KINGDOM.

Ionic polymer metal composites (IPMCs) are a class of materials composed of two high surface area metal electrodes deposited on either side of an ion exchange membrane. A range of these materials have been produced through the reduction of a metal salt on the surface of a Nafion membrane or by the deposition of an ink composed of nanoparticulate powder mixed with Nafion solution. The best results are obtained when the electrodes are composed of gold, although good results are also obtained when platinum is used. Electrodes composed of lead or cadmium show reasonably good results, although suffer from long-term stability problems. Electrodes composed of carbon work, although suffer from large resistive drops in the electrode layers. All of these materials show very high metal:Nafion interfacial contact areas, equivalent to roughness factors of several hundred. The IPMCs flex in both air and water when a potential of 2-4 V is applied across the two sides. In this paper we produce a range of IPMCs of different thicknesses and examine the force developed by these materials, the time constant of the flexing response and efficiency for converting electrical energy into work. The force developed by these materials at constant applied potential increases linearly with the thickness of the material over the range 70-440 μm . Efficiency of electrical to mechanical work is low, less than 1%, although this appears to be dominated by irreversibility in the electrochemical reactions occurring on the electrodes and resistive losses in the electrode layer.

This work was in part supported by Dr. Alan Hooper of QinetiQ plc [formally the UK Defence Research and Evaluation Agency] and funded through the UK MoD TG04 Materials and Structures Corporate Research Programme.

9:45 AM EE4.4

CHARACTERIZATION OF THE ELECTROMECHANICAL PROPERTIES OF IPMC. Yoseph Bar-Cohen, JPL, Pasadena, CA; Kaushik Bhattacharya, Caltech, Pasadena, CA; Xiaoqi Bao, JPL, Pasadena, CA; Shyh-Shiuh Lih, JPL, Pasadena, CA; and Xiao Yu, Caltech, Pasadena, CA.

Ionic Polymer-Metal Composite (IPMC) as electroactive polymer (EAP) was the subject of research and development since 1992. IPMC's low required activation voltage and the large bending led to the considerations of various potential applications. However, before the benefits of IPMC can be effectively exploited for practical use, the electro-mechanical behavior must be properly quantified. An experimental setup was developed for data acquisition from IPMC strips subjected to various tip mass levels and in parallel an analytical model was developed to predict the material response. Using the analytical model and an inversion algorithm the modulus, and relaxation time were determined. The programmable setup was used to acquire the displacement and curvature of IPMC as a function of the electrical signal characteristics. Sample strips were immersed in water to minimize the effect of moisture content and were tested with and without tip mass. In order to avoid hydrolysis the samples were subjected to 1-V square wave with either positive or negative polarity. A multi-scale model was developed that showed satisfactory results for tetra-n-butylammonium cations/Flamion IPMC, which responds slowly and monotonically without relaxation. This model starts at the mesoscale level with three fully coupled partial differential equations in cation concentration, electric potential and elasticity. Solution in the strip geometry leads to a macroscopic ordinary differential equation whose solution fits the observed behavior very well. Deviation from the model was observed when the material shows relaxation, as in the case of Li cations/Nafion. This type of IPMC has history dependence and responds with a quick bending that in fractions of a second starts relaxing and address this deviation would require further studies.

10:00 AM EE4.5

SHAPE MEMORY BEHAVIOR OF MODIFIED POLYCYCLO-OCTENE. Changdeng Liu, Seung-Bum Chun, Patrick T. Mather, University of Connecticut, Polymer Program and Chemical Engineering Dept., Storrs, CT; E. Bryan Coughlin, University of Massachusetts, Polymer Science and Engineering, Amherst, MA.

Shape memory materials are those that, after deformation to a different shape at certain conditions and fixing, can recover the original shape ("memory") by heating to a critical temperature. While the most common shape memory material is nitanol, a shape memory alloy (SMA), recent years have led to the discovery and investigation of shape memory polymers (SMP). Such materials attract significant attention due to low cost, large strain to several hundred percent, and a broad range of transition temperatures compared with SMAs.

Examples of SMPs include polynorbornene, polystyrene-*b*-butadiene, polyurethane, and trans-polyisoprene. In this presentation, we report on extensive thermomechanical characterization of a shape memory polymer we have recently developed - a modified polycyclooctene - that acts as a shape memory rubber (SMR). Quantitative assessment of strain recovery reveals a fast shape memory effect of the new materials whose rate is controlled by the material's microstructure. We present results of SMR characterization by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and wide-angle x-ray scattering (WAXD) and the mechanism of the shape memory is discussed in detail.

10:45 AM EE4.6

FACTORS AFFECTING ACTUATION RATE IN PARTIALLY NEUTRALIZED POLYELECTROLYTE GELS. Ingrid A. Rousseau, Kimberly G. Ozkan and Patrick T. Mather, Polymer Program and Chemical Engineering Dept., University of Connecticut, Storrs, CT.

Polyelectrolyte networks composed of poly(acrylic acid) (PAAc) cross-linked with poly(ethylene glycol dimethacrylate) are sensitive to electrical stimuli, allowing potential use as soft actuators. In our studies, PAAc was prepared via radical polymerization using UV irradiation from pregel solutions that allow independent control of the crosslinking density, the extent of neutralization, as well as the water content after polymerization. The networks thus formed underwent a swelling process that consists of, first, a soaking in deionized water to allow for the removal of the unreacted species, followed by several soakings in deionized water to reach swelling and pH equilibrium in the swelling bath. The bending behavior of these swollen PAAc hydrogels was studied under the influence of a DC electric field when applied either in deionized water, in the swelling medium at equilibrium, or in solutions of various pH. We find that the curvature observed for these hydrogels depends strongly on all of the chosen variables and that a compromise of low hydrogel neutralization and high pH of the surrounding medium yields the fastest electrical response. However, an unexpected phenomenon is also observed: the bending behavior seems to be composed of three stages that are active over differing time-scales. The earliest stage consists of a curvature toward the anode, and is followed by an intermediate stage that reverses the bending direction to be toward the cathode. Finally, the last stage features hydrogel rod shrinkage in all the directions. Depending on the conditions of our electromechanical analyses, the earlier and intermediate stages are more or less improved in terms of fast response and/or higher curvature attained. In order to evaluate the potential of those gels for eventual further applications, clarity as well as rheological measurements have been performed. Furthermore, the field-sensitive response of the gels was considered for both microporous and thin fiber-reinforced hydrogels.

11:00 AM EE4.7

MECHANICAL PROPERTIES CHARACTERIZATION AND MODELING OF ACTIVE POLYMER GELS. Steven P. Marra, K.T. Ramesh, Andrew S. Douglas, The Johns Hopkins University, Department of Mechanical Engineering, Baltimore, MD.

Active polymer gels expand and contract in response to certain environmental stimuli, such as the application of an electric field or a change in the pH level of the surroundings. This ability to achieve large, reversible deformations with no external mechanical loading has generated much interest in the use of these biomimetic gels as actuators and "artificial muscles." A thermodynamically consistent finite-elastic constitutive model was developed to describe the mechanical and actuation behaviors of active polymer gels. The mechanical properties are characterized by a free-energy function, and the model utilizes an evolving internal variable to describe the actuation state. Poly(vinyl alcohol)-poly(acrylic acid) (PVA-PAA) gel was chosen as the model material for this work because it is relatively simple and safe to both fabricate and actuate. These gels expand when moved from acidic to basic solutions, and contract when moved from basic to acidic solutions. The form and parameters of the free-energy function for fully contracted and fully expanded PVA-PAA gel were determined from uniaxial tests, and the evolution law for the internal variable was determined from free actuation experiments. The full constitutive model is used to predict the response of the PVA-PAA gel to isotonic and isometric loading and actuation. The model is shown to give relatively good agreement with experimental results.

11:15 AM EE4.8

MULTIFUNCTIONAL ELECTROELASTOMER ROLLS. Qibing Pei, Ron Pelrine, Scott Stanford, Roy Kornbluh, Marcus Rosenthal, Kenneth Meijer*, Robert Full*, SRI International, Menlo Park, CA; *Department of Integrative Biology, University of California, Berkeley, CA.

We will present multifunctional electroelastomer rolls (MER's) exhibiting high force, stroke, and strain sensor functions. The MER's are useful in a variety of applications where compact and high-stroke

actuation is required. Simulation results of a six-legged robot using the MER's as the robot's one-degree-of-freedom legs are described. The simulation is inspired by biological systems with the goal of producing a "synthetic bug" that can run and clear obstacles.

11:30 AM EE4.9

OPTIMAL DESIGN OF ELECTROSTRICTIVE COMPOSITES. Jianguo Li, Department of Engineering Mechanics, University of Nebraska, Lincoln, NE.

Electrostrictive response is inherent in any materials, but usually is too small for practical applications. Recently several polymer systems with high electrostrictive strain have been demonstrated. One approach to significantly enhance the electrostrictive strain is to increase the dielectric constant of polymer, which could be achieved using composite technology by adding a high-permittivity second phase. Care must be taken, however, to keep a balance between the increase of dielectric constant which tends to increase the electrostrictive strain, and increase of elastic constants which tends to decrease the electrostrictive strain. We propose a micromechanical approach for optimal design of electrostrictive composites, where the connection between macroscopic properties of composites and their microstructural details will be established. The optimal volume fraction and morphology of the second phase will then be identified, depending on whether the maximum electrostrictive strain or maximum strain energy is desired.

11:45 AM EE4.10

PHASE BEHAVIORS OF PARTIALLY IONIZED HYDROGEL PARTICLES IN AQUEOUS SALT SOLUTIONS: APPLICABILITY OF MODIFIED DOUBLE LATTICE THEORY. Young Pyo Hong, Young Chan Bae, Hanyang Univ, Division of Chemical Engineering, Seoul, KOREA.

Temperature and pH sensitive hydrogels play an important role in the application of biotechnology, pharmacy and medicine. But for successful applications, responses to same stimuli need to be quick and uniform. Thermodynamically, the swelling equilibrium of gels bounded ions is governed by the osmotic pressure of mixing, elasticity and difference of concentration of mobile ions between in gels and surroundings. Recently, Hu et al. reported the double lattice model to predict phase behaviors for polymer solution systems. In their model, ordinary polymer solutions are described by the primary lattice while the secondary lattice is introduced as a perturbation to account for the specific interaction. To predict successfully phase behaviors of poly-electrolyte hydrogels, we combined modified double lattice model (MDL), Flory and Erman's theory of elasticity and ideal donnan theory. Flory and Erman considered the elastic contribution to the change of the free energy due to isotropic swelling or shrinking as a rubber elasticity theory, which takes accounts of the nonaffine displacements of network junctions under strain. In this study, we modify Hu et al's double-lattice model by introducing new universal constants and simplifying the expression of the Helmholtz energy of mixing. Interaction parameters obtained from LLE data of the linear PNIPA/Water system are directly used to predict the swelling equilibria for the NIPA gel/Water systems and for cationic NIPA gel/water systems. Swelling behaviors are examined by using photon correlation spectroscopy (PCS) technique.

SESSION EE5: NOVEL ELECTROACTIVE POLYMERS III

Chairs: Eiichi Fukada and Yoseph Bar-Cohen
Tuesday Afternoon, November 27, 2001
Fairfax (Sheraton)

1:30 PM *EE5.1

UNDERSTANDING THE ROLE OF CURING HISTORY ON THE POLING AND PIEZOELECTRIC RESPONSE OF AMORPHOUS POLYIMIDE FILMS. Kristopher E. Wise, NRC/NASA-LaRC, Hampton, VA; Cheol Park, ICASE/NASA-LaRC, Hampton, VA.

Maximizing the piezoelectric response of amorphous polymer materials depends critically on the extent of polarization achieved during the poling procedure and on its retention after the field is removed. High temperature polyimide polymers are characterized by relative low rotational mobility along the backbone. This has the desirable effect of increasing their operational temperature and the undesirable effect of making them much more difficult to pole. Using a combination of theory and experiment, we have investigated a procedure in which partially cured polymers are poled prior to the final imidization reaction. Films produced in this manner exhibit increased piezoelectric properties and high thermal stability.

2:00 PM EE5.2

HETEROGENEOUS SPACE CHARGE ELECTRETS: MATERIALS

WITH LARGE AND BROADBAND PIEZOELECTRICITY.
Siegfried Bauer, Simona Bauer-Gogonea, Mario Dansachmüller,
Reinhard Schwödauer, Applied Physics, Johannes Kepler University,
Linz, AUSTRIA.

Piezoelectricity is an electromechanical effect describing the coupling between mechanical and electrical fields. Nowadays piezoelectricity is at the heart of a large number of applications, requiring sensitive and low-cost piezoelectric materials. Strong piezoelectric responses have been found in ferroelectric crystals, ceramics, and polymers. The piezoelectric response of ferroelectric polymers is only moderate in comparison to crystals and ceramics. Since several applications require low-density piezoelectric materials, with an acoustic impedance matched to air or water, the development of new piezoelectric polymers is a matter of urgency. It is shown that piezoelectricity is possible in space-charge electrets with quasi-permanent excess charges and heterogeneous material properties. A major breakthrough in the field has been independently reported most recently by several groups. Material heterogeneity combined with electrical charging offers new non-conventional routes for symmetry breaking and for the preparation of piezoelectric materials with tailored piezoelectric properties. Here we report on the piezoelectric response of charged, microporous closed-cell polypropylene foams and charged fluoropolymer hybrid materials, both showing excellent piezoelectric coefficients. It is shown that these unusual piezoelectric materials yield electrical responses that cannot be distinguished from true piezoelectricity. The strong piezoelectricity is coupled with weak pyroelectricity, an ideal combination for piezoelectric applications, since the piezoelectric response is not disturbed by spurious pyroelectric signals. Further developments and improvements in the piezoelectric properties of heterogeneous space-charge electrets seem possible, as discussed with simple theoretical models. In summary, the application of these ideas should provide a broad class of sensitive and easily fabricated 'soft' piezoelectric materials. Work supported by the Austrian Science Funds. Thanks are due to Drs. J. Lekkala and M. Paaanen, VTT Chemicals, Tampere, Finland for the excellent cooperation on the polypropylene foam.

2:15 PM *EE5.3
THERMALLY STIMULATED CURRENT ANALYSIS OF POLYMERS. Kazuo Ikezaki, Keio Univ, Dept Applied Physics and Physico-Informatics, Yokohama, JAPAN.

Thermally stimulated currents (TSCs) relating to the higher order structure of sample polymers are discussed. Because TSC in polymers is highly sensitive to their fine structure, it can be utilized to detect minute changes in the higher order structure of polymers that can not be detected by X-ray diffraction or differential scanning calorimetry. TSC studies were made for sample polymers with different higher order structures which were prepared by various methods: irradiation with pulsed laser light or ultrasound, spherulitic ordering, cross-linking and pulverization. Irradiation of polypropylene (PP) with CO₂ pulsed laser light produced crystalline defects in the polymer that act as deep charge traps and brought about local amorphization. Ultrasound irradiation of PP also induced the same changes as the case of laser light irradiation. TSC examination of spherulitic PP showed that spherulitic ordering drastically decreased the number of charge traps in the polymer. The TSC technique combined with visualization of charged areas also clarified that deep traps existed in the central parts of these spherulites and shallow traps in the interfacial and the peripheral regions of these spherulites. Three-dimensional networking in polymers by cross-linking greatly changes higher order structure of these polymers. The TSC method applied to evaluate the degree of cross-linking and its activation energy in powder paints for electrostatic powder coating. The TSC method also found applicable for powder-formed polymers. Pulverization of polymeres brings about large changes in their higher order structure due to rupture and/or disentanglement of polymer chains, and unfolding of crystalline lamera. From TSC results, the charge retention power of a binder resin for toners was found to decrease with decreasing particle size of the powder. Charge retention power of powder paints for electrostatic powder coating was also found to decrease even when they were stored at 50 C only for 10 min.

2:45 PM EE5.4
CHARACTERIZATION AND DEVELOPMENT OF P(VDF-TrFE) BASED HIGH PERFORMANCE ELECTROACTIVE POLYMERS. Dana Olson, H.S. Xu, Z.-Y. Cheng, Q.M. Zhang, Penn State Univ, Materials Research Laboratory, University Park, PA; R. Ting, Univ of Central Florida, Orlando, FL; T. Ramotowski, D. Hughes, G. Kavarnos, Naval Undersea Warfare Center, Newport, RI.

Recently, we reported the high electromechanical responses in the high energy electron irradiated copolymers. In this talk, we will present results from recent investigations on the microstructures and transitional behavior of irradiated copolymers. The data from synchrotron X-ray and FT-IR indicate that the defects introduced in

the irradiation process reduce the polarization coherence which eventually leads to the instability of the polar phase. The electric field induced transformation between the TG conformation and all trans conformation is responsible for the large electrostriction. Based on the understanding from the microstructure-functional property relationship, we further developed high performance electrostrictive PVDF based terpolymers, which eliminate the irradiation step and open up possibility of further improvement in the electromechanical properties of this class of polymers. We will present results demonstrate the importance in selecting 'right' ter-monomers to achieve high electromechanical responses and relate the responses in the terpolymers to the microstructures in the terpolymers. Experimental results show that, indeed, terpolymers exhibit much better electromechanical responses in comparison with the irradiated copolymers.

3:00 PM EE5.5
MOLECULAR MODELING STUDIES ON HIGH-STRAIN, ELECTROSTRICTIVE TERPOLYMERS. George Kavarnos, University of Rhode Island, Department of Chemistry, Kingston, RI; Thomas Ramotowski, Richard Hughes, Naval Undersea Warfare Center, Newport, RI; Qiming Zhang, Dana Olson, The Pennsylvania State University, Materials Research Laboratory, University Park, PA.

The finding that irradiation of copolymer films serves to break up the large crystalline regions into polar microregions resulting in a high-strain electrostrictive material has prompted an investigation to identify alternative routes to electrostriction. To determine whether these changes could be reproduced without the need for electron-irradiation, computations on PVDF-TrFE terpolymer chains containing small levels a third monomer incorporating chlorine have provided a theoretical framework to support the hypothesis that the introduction of chlorine in the polymer chain can produce similar structural defects that disrupt the polar all-trans regions into smaller regions. These calculations demonstrate that polar nano-regions can be created since introduction of bulky chlorine atoms into the polymer chains creates conformational defects that provide the mechanism to break up the long-range crystalline regions. The disrupted polar regions can be regarded as distorted defect structures that give rise to random fields and electrostriction. Theoretical predictions as well as experimental support will be presented that show that certain chloro-monomers such as -CFCl-CH₂- are indeed quite able to convert P(VDF-TrFE) films into high-strain, electrostrictive films.

3:45 PM EE5.6
CHEMICAL AND PHYSICAL CHANGES ASSOCIATED WITH HIGH-STRAIN ELECTROSTRICTION IN BETA-IRRADIATED PVDF-TrFE COPOLYMERS. Thomas Ramotowski, O. Richard Hughes, Naval Undersea Warfare Center, Newport, RI; George Kavarnos, University of Rhode Island, Kingston, RI; Karen Gleason, Massachusetts Institute of Technology, Cambridge, MA; Qiming Zhang, Pennsylvania State University, University Park, PA; Robert Ting, University of Central Florida, Orlando, FL.

In 1998, Zhang et al. demonstrated that large doses of high-energy beta radiation could transform certain vinylidene fluoride-trifluoroethylene (PVDF-TrFE) copolymers into high-strain electrostrictors. Since that time, U.S. Navy researchers and their colleagues have been analyzing irradiated PVDF-TrFE copolymers to determine what physical and chemical changes were associated with the materials' desirable high-strain electrostrictor properties. The most obvious radiation-induced structural change is the introduction and retention of more gauche-type linkages in the PVDF-TrFE polymer chains at room temperature, as evidenced by DSC, infrared spectroscopy, and X-ray diffraction data. These additional gauche linkages function as defects in the long, all-trans sequences normally found in PVDF-TrFE copolymers and, in effect, break up those sequences into the nano-polar domains necessary for high-strain electrostriction. The key role played by the beta radiation in this scenario appears to be the introduction of certain chemical changes (pendant groups, cross-links, and carbon-carbon double bonds) that interfere with or prevent rotation along polymer backbone carbon-carbon bonds. By preventing rotation, these chemical changes serve to preserve a higher percentage of gauche linkages below the polymer's Curie temperature. TGA, TGA-MS, 19-F NMR, FTIR, and DMA data documenting the existence of these beta radiation-induced chemical changes have been collected and will be presented. This research has important implications for synthetic polymer chemists interested in improving the existing materials and/or creating new, high-strain polymeric electrostrictors with or without the use of beta radiation.

4:00 PM EE5.7
NEW FERROELECTRIC FLURO-TERPOLYMERS BASED ON VDF,TrFE,AND BULKY TERMONOMER; HIGH DIELECTRIC CONSTANT AND LARGE ELECTRIC RESPONSE AT AMBIENT TEMPERATURE. T.C. Mike Chung, A. Petchsuk, The Pennsylvania

This paper discusses a new family of ferroelectric polymers with high dielectric constant (> 50 at 1K-1M Hz) and large electrostrictive response ($>5\%$) at ambient temperature. These polymers are high molecular weight semicrystalline terpolymers comprising vinylidene difluoride (VDF), trifluoroethylene (TrFE), and a bulky third monomer, such as chlorotrifluoroethylene (CTFE). They were prepared by a living free radical initiator, based on the in situ oxidation adduct of trialkylborane/oxygen, and bulk polymerization process at low reaction temperature. The combination of living polymerization mechanism and monomer feeding control to maintain constant monomer feed ratio affords the terpolymers with the designed polymer molecular weight and relatively narrow molecular weight and composition distributions. The incorporated bulky third monomer units homogeneously distributed along the polymer chain seem to reduce the thickness of ferroelectric crystalline domains without destroying the overall crystallinity. This nano-size semicrystalline morphology results in the reduction of ferroelectric-paraelectric (F-P) phase transition to near ambient temperature with a very small energy barrier. Some terpolymers exhibited common ferroelectric relaxor behaviors with a broad dielectric peak that shifted toward higher temperatures as the frequency increased, and a slim polarization hysteresis loop at near the dielectric peak (around ambient temperature) that gradually evolved into a normal ferroelectric polarization hysteresis loop with reduced temperature.

4:15 PM EE5.8

MODEL DEVELOPMENT FOR HIGH-PERFORMANCE
PIEZOELECTRIC POLYMERS. Zoubeida Ounaies, ICASE, M/S
132C, NASA Langley Research Center, Hampton, VA; Ralph Smith,
Department of Mathematics, North Carolina State University,
Raleigh, NC.

Piezoelectric polymers have been incorporated as sensors and actuators in devices employed in applications ranging from biomedical imaging to flap design for flow control. An important emerging application area for electroactive polymers is in the biomedical field where polymers are being explored as potential artificial muscle actuators, actuator implants to stimulate tissue and bone growth, and sensors to monitor vascular grafts and to prevent blockages. Such applications are ideal for polymers since they have excellent conformability and impedance matching to body fluids and human tissue and they can be designed to be biocompatible. Polymers typically possess a high dielectric breakdown and high operating field strength, which means that they can withstand much higher driving fields than ceramics. Due to inherent properties, their behavior exhibits nonlinear and hysteretic effects which must be characterized to fully realize the potential of these materials in high performance applications. This work focuses on the characterization of fundamental properties of piezoelectric materials (e.g., PVDF), including molecular structure effects and constitutive nonlinearities, through a symbiotic combination of experimental and analytic techniques. Aspects of the model will be validated through comparison with experimental data.

4:30 PM EE5.9

Transferred to EE5.1