

with doping, while at the same time the activation energy decreased, reaching a low of 0.12 eV when every TMTPD molecule was oxidized. This behavior can be understood in terms of transport manifold filling, Coulombic trapping of charge, and broadening of the transport manifold due to dipolar disorder induced by the dopants.

K10.104

Development of Multifunctional Polymer Systems for Surface Molecular Imprinting Technology. Abdiaziz A Farah¹, Raluca Voicu¹, Pascal Lecuyer², Farid Bensebaa² and Karim Faid¹;
¹Institute of Microstructural Sciences, National Research Council of Canada, Ottawa, Ontario, Canada; ²Institute of Chemical Processing environmental & Technology, National Research Council of Canada, Ottawa, Ontario, Canada.

Molecularly imprinted polymers (MIPs) have recently emerged as a new research domain both in academia and in industry. A large variety of molecularly imprinted polymer systems have been reported in the literature for use in chemical separations and catalysis as well in biochemical and pharmaceutical applications. A new paradigm of molecular imprinting using surface characterization techniques in conjunction with a nanotemplating methodology will be presented. A surface-attached moiety is used as a stamp, and is contacted with a variety of functional monomers. Following the selective removal of the stamps, recognition cavities are created on a substrate surface and are found to be selective towards the moiety of interest. In this contribution, we report on the synthesis and characterization of a number of multi-functional polymers (i.e. poly(methacrylates) with both specific recognition sites and surface-attachable groups) that are used to incorporate a target molecules and form an artificial recognition cavity. Upon the transfer and attachment to a defined substrate, these artificial recognition cavities are used to selectively rebind the target molecules. Comprehensive solution and solid-state characterizations of the multi-functional polymers as well as the surface-anchored polymer nano-template will be presented, including 1H-NMR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), gel permeation chromatography (GPC), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared reflection-absorption spectroscopy (FT-IRRAS) and Scanning Probe Microscopy (SPM).

K10.105

Morphology Evolution in Nano-Scale Light-Emitting Domains in MEH-PPV/PMMA Blends. Nisha Ananthakrishnan, Benjamin Harrison, Randolph S Duran, Kirk S Schanze and John R Reynolds; Chemistry, University of Florida, Gainesville, Florida.

The effect of polymer blend composition and morphology on light emitting characteristics of MEH-PPV/PMMA blend films was investigated. The evolution of the microstructure from isolated light-emitting domains ranging in diameter from 300-900 nm and 100 nm thickness to a continuous light emitting material was seen as the composition of MEH-PPV in the blend film was increased. The 5 wt% compositional study was used to demonstrate stability of morphology, as identical structures were observed for the blend film dried in air, vacuum dried at room temperature and vacuum dried at 80 degC. A "phase inversion" is observed at approximately 50 wt% MEH-PPV where a bi-continuous network of the two polymers is observed. Results of AFM (topographic and phase images), bright field, fluorescence microscopy and the emission from LEDs using the bright field in fluorescence microscope are used to illustrate this morphological evolution. This study also demonstrated that the highest efficiency devices were obtained at 75 wt% MEH-PPV where a continuous light-emitting polymer structure surrounds isolated domains of PMMA.

SESSION K11: Optically Active Materials and Electronic Memories

Chairs: John Reynolds and Gordon Wallace
Friday Morning, December 5, 2003
Back Bay C (Sheraton)

8:30 AM *K11.1

Patterning Of Dioxathiophene Based Polymer Electrochromic Devices. John R Reynolds, Avni Argun, Pierre Henri Aubert, Mathieu Berard, Ali Cirpan, Carleton Gaupp, Christophe Grenier, Jessica Hancock, Benjamin Reeves and Irina Schwendeman; Chemistry, Univ. of Florida, Gainesville, Florida.

By controlling the electron-rich character and degree of pi-overlap along a conjugated polymer chain, a family of multi-colored electrochromic polymers has been developed. Within this, low band gap polymers provide cathodically coloring materials, while high band gap polymers provide anodically coloring materials. A broad spectral variation is accomplished via copolymer composition yielding films

whose colors range through yellow-orange-red-purple-blue, while controlled conductivity changes allow for infrared electrochromism. When complementary anodically and cathodically coloring polymer pairs are utilized in absorption-transmission configured electrochromic devices, large changes in visible light transmission can be rapidly modulated (sub-second switching). Patterned electrodes allow the construction of laterally configured electrochromic devices in which the reflectivity from metal surfaces can be modulated across a broad spectrum. Thin metal films as electrode contacts have been prepared using a combination of metal vapor deposition and line patterning methods yielding highly flexible electrochromic devices. Application of commercially available PEDOT/PSS as an electrode material has yielded the first truly all-polymer electrochromic devices. By careful control of polymerization conditions, electrochromic polymers prepared using commercially available monomers can be incorporated into relatively long-lived devices.

9:00 AM K11.2

Planar Polymer Light-Emitting Devices with Extremely Large Inter-electrode Spacing. Justin Dane and Jun Gao; Physics, Queen, Kingston, Ontario, Canada.

A polymer light-emitting electrochemical cell (LEC) offers an alternative approach to achieving electroluminescence (EL) from conjugated polymers. Unlike a polymer light-emitting diode (PLED), the operation of a LEC involves in situ electrochemical doping and the formation of a dynamic p-i-n junction. A LEC is relatively insensitive to the variations in device thickness (anode-to-cathode spacing). As a result, planar LECs (pLECs) have been demonstrated on pre-patterned substrates with micrometer inter-electrode spacing, and yet still have the same low turn-on voltage as a regular sandwich LEC only a few hundred nanometers thick. This suggests exploring the possibility of making pLECs with even larger inter-electrode spacing. Here we report pLECs with inter-electrode spacing up to 2 mm, nearly 100 times larger than previously demonstrated. These large pLECs offer a unique and, arguably, the most direct approach for polymer device research. High-resolution imaging of EL using only a digital camera reveals an extremely wide emission zone, indicative of a surprisingly inefficient recombination process in these polymer devices with balanced charge injection. Imaging under UV excitation reveals an electrochromic effect due to p-doping of the polymer film. The p-doped region migrates towards the cathode unevenly during operation, causing the emission zone at its frontier to shift and giving rise to its irregular shape.

9:15 AM K11.3

Electric field visualization within electrolytes using electrically isolated electrochromic polymer islands.

Nathanial D. Robinson, Elias Said, David Nilsson, Per-Olof Svensson, Jessica Hall and Magnus Berggren; Dept. of Science and Technology (ITN), Linköping University, Norrköping, Sweden.

The electric field within a 2-dimensional electrolyte can be visualized by applying the electrolyte over an array of dots of electrochromic polymer material (such as PEDOT:PSS) on a plastic foil and observing the color change within each polymer dot. The result is a vector-field analogous to that obtained by placing an array of iron pins in a magnetic field, except that this measurement also allows for the magnitude, as well as the direction, of the field to be measured at each location. The devices studied were created by etching

PEDOT:PSS on AGFA OrgaconTM foil leaving an array of small circles. Any method and reversibly electrochromic polymer could have been used. The electrolyte was then applied as a thin film on top of the foil. The measurement requires that an electric field be present within the electrolyte, which generally means that there is an ionic current. In the experiments presented here, a constant voltage was applied between an anode and a cathode while the field was visualized between the two. The visualization is based on the color change associated with the doping/de-doping within each electrochromic polymer dot in response to the voltage drop across the island. The whole device is then rasterized using a standard flatbed scanner and the resulting image analyzed. This device has direct applications as a method for electrolyte evaluation, but is also applicable in bio-analytical measurements and separations such as electrophoresis.

9:30 AM K11.4

Polythiophene Based Thermochromic Pigments: Control of Reversibility. Brett L Lucht, Yu Wang, Adrienne Marold, Nadia Archambault and William Euler; Chemistry, University of Rhode Island, Kingston, Rhode Island.

Thermochromic materials are used to provide a rapid, visual assessment of temperature. Currently available, commercially used reversible thermochromics are based on either liquid crystal technology or acid-base reactions. Both of these technologies have a variety of disadvantages including high cost, poor thermal and light stability, large particle size, and extractability. We report on the

development of new thermochromic pigments based on polythiophenes. There have been numerous investigations of the structure and organization of polythiophene films and the structural changes that occur during the thermochromic transition. The investigations have primarily focused on the behavior of these materials as pure films or in solution. However, the utilization of conjugated polymers as thermochromic pigments requires them to be dispersed in a host polymer matrix. There have been few investigations on the thermochromic properties of polythiophenes in host polymers. In this article we discuss an investigation of the structure, organization, and thermochromism of substituted polythiophenes as pure solids and as dispersions in host polymers. The host polymers of most interest include polystyrene, polycarbonate, and polyolefins. The generally accepted mechanism for the thermochromic transition is based on a two-step process. At low temperature the conjugated repeat units are in a planar conformation and the substituents of the polythiophene chain ordered into a lattice. As the temperature is raised, the side chain lattice melts and the resulting disorder allows the main chain repeat units to twist away from planarity. The twisting of the polythiophene units increases the band gap, resulting in a blue shift of the optical absorption. The melting of the sidechains causes a zipper effect, which results in a sharp thermochromic transition. However, the role of intramolecular aggregation in the thermochromic transition is unclear. We will discuss the investigation of the thermochromic properties of poly(3-alkylthiophene)s with reversible and controlled reversible thermochromic transitions. The investigation of the materials as both pure solids and as dispersions in commodity plastics has been conducted. The temperature of the thermochromic transition and reversibility of the transition is dependent upon the alkyl substituents but largely independent of host polymer. Poly(3-alkylthiophene)s with sharp thermochromic transitions between 40 and 140 °C have been prepared and investigated. The controlled reversibility of poly(3-alkylthiophene)s allows the reversible thermal marking. We will propose a mechanism for the observed controlled reversibility of poly(3-alkylthiophene)s.

10:15 AM K11.5

Carbon Nanotube Biofibres. Gordon George Wallace¹, Joseph Barisci¹, Simon Moulton¹, May Tahhan¹, Philippe Poulin², Stephane Badaire², Thibaud Vaugien² and Maryse Maugey²; ¹IPRI, University of Wollongong, Wollongong, New South Wales, Australia; ²Centre de Recherche Paul Pascal, CNRS, Pessac, France.

The assembly of fibres with appropriate mechanical and electronic properties combined with biofunctionality will impact on areas such as biosensors, bioseparations and new platforms for cell culturing and stimulation. In this work we present an exciting new development wherein biomolecules (e.g. DNA) have proven to be exceptional dispersants for single wall carbon nanotubes. These dispersants can subsequently be spun into a coagulation bath to produce CNT fibres with exceptional mechanical attributes as well as acceptable electronic and electrochemical properties. Our recent studies into the use of other biomolecules for fibre spinning will also be presented.

10:30 AM *K11.6

Electric-Field Effect Devices Based on Doped Conducting Polymers. Arthur J Epstein^{1,2}, Fang-Chi Hsu¹, Nan-Rong Chiou³, Oliver Waldmann¹, June Hyoung Park¹, Youngmin Kim¹ and Vladimir N Prigodin¹; ¹Physics, The Ohio State University, Columbus, Ohio; ²Chemistry, The Ohio State University, Columbus, Ohio; ³Chemical Engineering, The Ohio State University, Columbus, Ohio.

The field effect devices prepared using active channels fabricated from doped conducting polymers, such as PEDOT/PSS (polyethylenedioxythiophene/poly(styrene sulfonic acid)), polypyrrole Cl₁ and polyaniline with various dopants are reported. Normally in the "on" state, the devices have a sharp switch off at a small gate voltage. The current ratio Ion/Ioff/ can exceed 10⁴ at room temperature. The temperature dependence of the dc conductivity of the PEDOT/PSS follows the variable range hopping law both before and after application of the gate voltage. The activation energy, T₀, increases even for on/off ratios as small as 1.07 demonstrating that the electric field effect has changed the bulk charge transport in the active channel despite the expected screening due to mobile charge carriers. Based on these transport and optical studies we propose that the conducting polymer is near the metal-insulator transition and that the field effect in the transistor is related with electric field modulating this transition in the region underneath of gate through field induced ion motion. The time dynamics of current with the gate modulation strongly supports our proposal. We demonstrate fabrication of inverter, amplifier and nonvolatile memory circuits based on these field effect devices. Application of the Doped Polymer Field Effect Devices (DPFEDs) to memory, amplifier and other devices will be discussed. Supported in part by Office of Naval Research.

11:00 AM K11.7

Conductive Electrochromic Polymers as Electrochemical Fuses for Hybrid Inorganic/Organic Semiconductor Memories. Sven Moller¹, Stephen Forrest¹, Craig Perlov², Warren Jackson² and Carl Taussig²; ¹Princeton University, Princeton, New Jersey; ²Hewlett-Packard Labs, Palo Alto, California.

We demonstrate a non-volatile, write-once-read-many-times (WORM) memory device employing a thin film silicon diode on a flexible substrate integrated in series with a conductive polymer fuse. The nonlinearity of the silicon diode enables a large scale passive matrix memory configuration, while the conductive polyethylenedioxythiophene:polystyrene sulfonic acid (PEDT:PSS) polymer acts as a switch with fuse-like behavior for data storage. The polymer can be switched within 2 microsec, resulting in a permanent increase of resistivity of the memory pixel up to a factor of 1000. We analyze the switching mechanism and find that while it is primarily due to current-induced redox reactions in the polymer, it also depends on electric field and thermal activation of the conductivity switching process. The switching effect performance is highly reliable in its operation, and the fuses do not degrade after many thousand read cycles in ambient at room temperature. To our knowledge, this reports the first demonstration of permanent non-destructive conductivity switching in a conductive polymer. Given these results, very high performance, low cost, lightweight archival hybrid inorganic/organic WORM memories for video image and other archival storage applications are feasible.

11:15 AM *K11.8

High Performance Organic Memory Device. Yang Yang, Jianhua Wu, Jun He, Liping Ma and Qianfei Xu; Materials Sci. & Eng., UCLA, Los Angeles, California.

In this presentation, we present our latest study of high performance organic memory device and its theoretical modeling. The device structure is organic/metal/organic tri-layer sandwiched between two metal electrodes. When the metal nano-particle layer is presented within the organic layer, the density-of-states (DOS) has a dramatical change. For pure organic material, the DOS is mainly located near the LUMO and HOMO levels. Hence, the probably for charge transmission from the Al electrode into the organic layer is small, due to the mis-match of Al Fermi level and the DOS of organics. However, the DOS of the nano-particle layer is located in the mid-gap state. When the nano-particle layer is charged, the charge transmission probability enhanced several orders of magnitude. As a result, the device conductivity also enhances several orders of magnitudes. This study clearly explains the importance of the nano-particle layer and device operating mechanism. 9/9/03 Changed from invited to oral per Symposium Organizer, G. Jabbour.

11:45 AM K11.9

A Low-Voltage Rewritable, Spincast Organic Memory Device. Ronald C.G. Naber¹, Paul W.M. Blom¹ and Alwin W. Marsman²; ¹Materials Science Centre, University of Groningen, Groningen, Netherlands; ²Philips Research Laboratories, Eindhoven, Netherlands.

Ferroelectric copolymer films of poly(vinylidene fluoride/trifluoroethylene) are used for many applications such as microphones and actuators. Another interesting use is to integrate the material into a field effect transistor to make a nonvolatile memory device. By combining current efforts to make patterned PEDOT:PSS electrodes and to find high-performance polymer semiconductors, one could conceivably make an all-organic NVRAM by spincasting only. The major problem with the applicability of P(VDF/TrFE) is the high voltage needed to switch the remanent polarization. This voltage can be lowered by using very thin films (<100 nm), but reported results on thin films gave an inferior ferroelectric response so far. In dissimilar capacitor devices, with active layer thicknesses of only a few tens of nanometers, we were able to reduce the switching voltages down to 2 Volts and still maintain a remanent polarization only slightly less than the bulk value (~40 mC/m² for the 50/50 copolymer).

SESSION K12: Active Materials
Chairs: Vladimir Bulovic and Aimee Rose
Friday Afternoon, December 5, 2003
Back Bay C (Sheraton)

1:30 PM K12.1

Chemosensing Lasing Action In Conjugated Polymers. Aimee Rose^{1,2}, Zhengguo Zhu¹, Conor Madigan², Timothy Swager¹ and Vladimir Bulovic²; ¹Chemistry, MIT, Cambridge, Massachusetts; ²Laboratory for Organic Optoelectronics, MIT, Cambridge, Massachusetts; ³MIT, Brookline, Massachusetts.

Previous work in our group has demonstrated the bright fluorescence

of electron rich conjugated polymers is significantly attenuated upon exposure to electron deficient aromatic analytes such as trinitrotoluene (TNT). The mechanism responsible is most likely an electron transfer event from the excited state of the polymer to the lowest unoccupied molecular orbital (LUMO) of the particular analyte. Hence, electrostatics dictate to which compounds a particular polymer will respond. With careful design of novel fluorescent conjugated polymers, responses to attograms of TNT can be measured. It has also been well established that conjugated polymers can exhibit stimulated emission when optically pumped with high energy excitation. Stimulated emission is very sensitive to any type of competitive process; non-radiative decay of excited states can increase the threshold for observation of stimulated emission and even prevent it entirely. Because sensitivity of these materials to TNT results from induced non-radiative decay, exposure to TNT near threshold should therefore prevent stimulated emission at that input energy. This approach to detecting TNT and other electron-deficient analytes offers unprecedented enhancement in sensitivity. Stimulated emission is a non-linear process therefore output intensity increases exponentially with input power once lasing threshold has been reached. Attenuation of this signal when compared to the spontaneous (linear) emission response is inherently more sensitive since signal-to-noise of the emission measurements can be improved by orders of magnitude. In addition, we have demonstrated that stimulated modes of emission are more significantly attenuated upon analyte exposure than their spontaneous counterparts. This enhanced quenching coupled with improved emission intensity signal-to-noise provides a significant and novel enhancement in sensitivity over what is observed below lasing threshold. *Presenting/ Contact Author Aimee Rose Physical Science Inc 20 New England Business Center Andover MA 01810 Ph. 987.689.0003 Fax 987.689.3232 arose@alum.mit.edu

1:45 PM K12.2

Design of Organic Star-shaped Electro-optic chromophores: Synthesis and Correlation of Guest-host Morphology with Electro-optic Activity. Padma Gopalan, Howard Edan Katz and David J McGee; Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey.

Azo-benzene based push-pull chromophores with dendritic architecture were synthesized as active materials for electro-optic applications. These chromophores were synthesized in 6 to 7 synthetic steps with an average yield of 60-80% per step and high purity. STEM analysis of the blends of chromophores with polymer host enabled the correlation of the activity of these large chromophores with the blend morphology. Amorphous polycarbonate host effectively disperses the chromophores in 2–20 nm aggregates in the active materials. However, macrophase separation into 200–500 nm aggregates was observed in the methacrylate host matrix. UV-Vis spectroscopy showed significant influence of the transient dipole moment to the observed r_{33} values. These chromophores were stable to photochemical oxidation in ambient light and air. The electrical poling conditions were optimized for each chromophore as the T_g of the composite material varied significantly. The highest EO coefficient achieved was 22–25 pm/V at 1550 nm wavelength.

2:00 PM K12.3

The study on new organometallic complex crystals with high second- and third- nonlinear effects. Dong Xu¹, Guang hui Zhang^{1,2}, Xin qiang Wang¹, Yak tak Chow², Xie ning Jiang¹, Meng kai Lv¹ and Duo rong Yuan¹; ¹State Key Lab. of Crystal materials, Shandong University, Jinan, Shandong, China; ²Optoelectronics Research Centre, City University of Hong Kong, Hong Kong, China.

In this paper New Organometallic complex crystals using for doubling of diode laser or all optical switch is reported. Over 10 mw violet at 404 nm has been achieved by ZCTC crystal; Some of ET derivatives may possess much higher nonlinear coefficient than that of organic materials. Previous studies with respect to nonlinear optical material have mainly focused on inorganic oxide or conjugated organic molecular system, while on the contrary, our attention has been paid to organo-metallic complex compounds, which structures not only have coordinating polyhedron in geometry like in oxide crystals, but also possess conjugated planar molecules or radicals like in organic crystals. The structural characteristic may make organometallic complex crystals improving and adjusting some properties of inorganic or organic crystals. The efforts on organic semiconductor with non-central symmetrical structure and high mobility is very important for exploring new nonlinear optical materials used in many application of photo-electronic devices with fast response. ZnCd(SCN)₄ (abbreviated as ZCTC) crystal, one of bimetallic thiocyanate complex crystals with ABTC structure type, is chiefly nonlinear optical material for realizing blue-violet light output by laser diode frequency-doubling. Main parameters of ZCTC and various common crystals were shown in Table.1. The decomposing temperature is up to 234^o C , UV cutoff is 290 nm, the factor of merit is higher than that of KTP, BBO crystal. The growth morphology and mechanism have

also been investigated by AFM, the defects are mainly caused by liquid inclusions, which are formed due to instability of step bunches and macro-steps in ZCTC crystals, and hole bunches oriented along b-axis direction have also discovered. The results are useful to guide the practical crystal growth process. Another kinds of organometallic nonlinear materials is several derivatives of BEDT-TTE (abbreviated as ET). The design, synthesis, growth and characterization of some nonlinear optical materials chosen have been paid into large attention and in process. The structural features resulted in fact that nonlinear coefficient, especially Third-order effects, may be much higher than that of organic or polymer materials. Table 1. Main Parameters of ZCTC and Various Common Crystals

2:15 PM K12.4

Azo Polymers Containing Two Types of Main Chain Units for Thick Holographic Media. Jiro Minabe, Tatsuya Maruyama, Katsunori Kawano, Shin Yasuda, Kazuhiro Hayashi and Yasuhiro Ogasawara; Corporate Research Lab., Fuji Xerox Co., Ltd., Kanagawa, Japan.

Polymers with azobenzene side groups have attracted much attention as materials for holographic storage. Optically induced birefringence in the azo polymer films contributes to formation of holograms. Volume holographic storage requires thick media (> 200 μ m) to achieve high storage density. However, it is difficult to fabricate the thick azo polymer films compatible with low-scattering noise, high photosensitivity and high stability of data. In general, amorphous polymers exhibit low-scattering noise, but magnitude and stability of the birefringence leave room for improvement. On the other hand, semicrystalline polymers have the large and stable birefringence, but they have high-scattering nature. To utilize the advantages of both types of polymers, we controlled crystallinity of azo polyester by changing the copolymerization ratio of two types of main chain monomers: The polyesters were synthesized with 6,6'-(4,4'-oxydiphenylenedioxy) dihexanol (OPOH), 6,6'-(4,4'-sulfonyldiphenylenedioxy) dihexanol and diethyl isophthalate containing a side chain unit. The polyesters with OPOH of 0 mol% and 100 mol% are amorphous and semicrystalline, respectively. Among six kinds of the polyesters with various OPOH ratios, the polyester with OPOH of 90 mol% exhibited the best performance: (i) The optically induced birefringence was maximized. (ii) The birefringence relaxation after the recording was 5 %. It was one eighth of that for the amorphous polyester with 0 mol%. (iii) A low-scattering film of 250 μ m in thickness was easily prepared by heating and quenching processes, while the film of the semicrystalline polyester with 100 mol% was not. (iv) The exposure energy for the diffraction efficiency of 20 % was 20 J/cm². It was one sixth of that for the film of the amorphous polyester with 0 mol%. Thus, the copolymerization with two kinds of main chain monomers is an effective method of designing the azo polymer film for volume holographic storage.

2:30 PM K12.5

Fabrication of a Urea Sensor on a Biologically Derived Plastic. Terri Wilson¹, Emmanuel P Giannelis², Carl A Batt³, Nuttawee Niamsin³, K V Madanagopal⁴ and Scott J Stelick⁴; ¹Chemical & Biomolecular Engineering, Cornell University, Ithaca, New York; ²Materials Science & Engineering, Cornell University, Ithaca, New York; ³Food Science, Cornell University, Ithaca, New York; ⁴Alliance for Nanomedical Technologies, Ithaca, New York.

A novel class of nanofabricated biosensors on a biodegradable platform is being developed. They consist of interdigitated microelectrodes, with a gap size and electrode width of 50 micrometers, evaporated onto polyhydroxybutyrate, a biologically derived plastic film, which is also biocompatible. The target analyte, urea or glucose, is detected conductimetrically by monitoring the change in conductance during their enzymatic hydrolysis. The functionalization of the microelectrodes is accomplished by either immobilization of the enzyme in a sol-gel matrix or direct attachment using appropriate surface chemistry. A microfluidic device has been integrated with the sensor containing microfluidic channels made of a polydimethylsiloxane/polyhydroxybutyrate hybrid. In this talk we will present the fabrication methods, miniaturization efforts including developing a hand-held device, and the biosensor's application to the conductimetric detection of glucose and urea.

2:45 PM K12.6

Photoaddressable Block Copolymers for Holographic Data Storage - Synthesis Properties and Applications. Hans-Werner Schmidt¹, Carsten Frenz¹, Thomas Breiner¹, Ulrich Theissen² and Dietrich Haarer²; ¹Makromolekulare Chemie I, Universitaet Bayreuth, Bayreuth, Germany; ²Experimental Physik IV, Universitaet Bayreuth, Bayreuth, Germany.

Light-induced reorientation of azobenzene chromophores in polymers has been subject of intense chemical and physical research in the past 20 years. For example the materials properties and their orientation

dynamics were investigated as a function of spacer length, content and nature of the azo-chromophore. Our study is based on an additional concept, the geometrical constraint imposed by introducing the azobenzene sidegroups into microphase-separated domains of a block copolymer. First examples of such block copolymers are described by Mao et al., [1] who attached azo sidegroups to an isoprene backbone in a block copolymer with polystyrene as matrix. We present in this contribution several homopolymers and block copolymers synthesized by living anionic polymerization. As a strategy to obtain the final homopolymers and block copolymers an optimized polymeranalogous reaction was applied. For example, in one series block copolymers based on poly(styrene)-block-poly(butadiene) with a high degree of 1,2-polydiene content were synthesized. The polymerization was carried out in analogy to the procedure developed by Saenger et al. [2] The polydiene-block was functionalized by a hydroboration reaction to generate a poly(1-butene-4-ol) block which was suitable for the further polymeranalogous reactions. Another block copolymer system consists of poly(methylmethacrylate)-block-poly(hydroxyethyl-methacrylate) which was synthesized by sequential anionic polymerization. T-butyl-dimethyl-silyl as a rather stable protection group [3]-for HEMA was selected [4]. Various azobenzene chromophores with reactive acid chloride groups were synthesized and attached to the backbone. The resulting polymers were characterized by DSC, TGA and SEC measurements. The morphologies were investigated by TEM and AFM measurements. Thin films (1 mm to 20 mm) and thick samples (500 mm to 1 mm) were prepared and investigated by means of transmission holography. The holograms are written with a wavelength slightly higher than λ_{max} of the absorption band (488 nm or 532 nm) and read out at a wavelength outside of the absorption band (685 nm). The writing beams induced a reorientation of the chromophores resulting in an anisotropy of the refractive index which is detected by the reading beam. We measured the evolution time of the refractive index within thin and thick samples focusing on the orientation and relaxation dynamics of the chromophores within different morphologies. For thick samples we achieved an angular multiplexing with a resolution down to 0.2 degree. [1] G. Mao, J. Wang, C. K. Ober, J. T. Chen, E. L. Thomas et. al., *Macromolecules* 30 (1997) 2556 [2] J. Saenger, C. Tefehne, R. Lay, W. Gronski, *Polymer Bulletin* 36 (1996) 19 [3] A. Hirao, H. Kato, K. Yamaguchi, S. Nakahama, *Macromolecules* 19 (1986) 1294 [4] T. Breiner, H.-W. Schmidt, A.H.E. Mueller, *e-Polymers* No. 22 (2002)

3:30 PM *K12.7

Electronic Transport Properties of Molecular Structures from Mixed-Valence Model Compounds to Single Molecules and Beyond. Marcel Mayor, Institut für Nanotechnologie, Forschungszentrum Karlsruhe, Karlsruhe, Germany.

Electron transport through molecular structures is investigated in detail by different methods, and correlations between molecular structures and transport properties are the focus of the presentation. The potential of rigid π -systems to act as molecular wires was explored. Reducible units (polythiophenylbenzenes) were connected by the structural motives of question and the resulting dimer-like structures were investigated by electrochemical methods. To examine the potential of the most promising molecular wire motive the diacetylene connector in further detail, longer rigid-rod like structures and cyclic compounds consisting of diacetylene connected poly-thiophenyl substituted benzenes were synthesized as model compounds and studied by electrochemical and optical methods. While para diacetylene substituted benzenes are communication active connectors, meta diacetylene substituted benzenes turned out to be passive ones. The resulting molecular structure vs. knowledge of electron transport properties allowed to synthesize tailor-made rod-like structures to be investigated as bridging molecules between two electrodes. Comparison of the I/V characteristics with the symmetry of the studied molecules provided first indications, that single molecules can be immobilized and studied between two gold electrodes. Further work was focused on tuning the resistance of the set-up by varying the molecular structure. For instance, the potential of a platinum(II) complex as single molecule insulator could be shown. Finally, the above gathered electronic skills of molecular structures allow the design of new nano-scale objects with tailor-made physical properties. As a first example, a giant cyclic molecule is designed and synthesized that fulfills all requirements to observe persistent currents in molecular structures.

4:00 PM K12.8

Computer Designed, Molecularly Assembled Rugate Filters. Adam J Nolte¹, Michael F Rubner¹ and Robert E Cohen²; ¹Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Earlier work has confirmed the possibility of using the polyelectrolyte multilayer (PEM) deposition technique with subsequent in situ nanoparticle synthesis to create optical interference coatings. Such

coatings are generally based on alternating layers of quarterwave optical thickness, and demonstrate interesting optical characteristics, such as tunable reflection and pass bands. The desire to extend this technique to filters possessing arbitrary variations in refractive index (rugate filters) is motivated by the ability to enhance the optical filter performance. Such enhancements can include the narrowing of reflection bands and the elimination of higher order reflectance lobes. This talk will discuss the unique way PEMs are suited to creating rugate filters through "digitization" of the continuous index profile design, whereby the sequential thickness control of numerous discrete high index and low index layers is used to approximate a smooth refractive index profile. Spectroscopic results obtained following the construction of a PEM-based apodized rugate filter confirm the presence of a high reflection band with minimal sidelobe reflectances, while cross-sectional TEM reveals the enabling microstructure and highlights the precise nanoscale control that PEM-templated nanoparticle synthesis offers the materials designer.

4:15 PM K12.9

Carbon Nanotube Actuators and Sensors. Alan Dalton, Steve Collins, Edgar Munoz, Ali Aliev, Dong-Seok Suh, Joselito M Razal, Mike Koslov, Satish Karsala, Anvar A Zakhidov and Ray H Baughman; NanoTech Institute, University of Texas @ Dallas, Richardson, Texas.

Porous single wall carbon nanotube arrays have been fabricated in the form of sheets and fibers. Utilizing this porosity and the high surface area of carbon nanotubes, we find that these assemblies can act as smart noses or tongues that respond to chemicals by actuating like muscles. We use this chemically induced actuation to make cantilever actuators which use the differential expansion of opposite sides of film strips to cause actuation by sheet bending. Electron microscopy, Raman scattering and x-ray diffraction are used to characterize the actuating assemblies. The origin of this phenomenon is discussed in relation to charge injection, interfacial stresses and overall growth of the nano-fiber diameter as a consequence of adsorption of a chemical on the surfaces of nanotube bundles. Possible applications are discussed.

4:30 PM K12.10

Integration of visible and IR-active semiconductor nanocrystals with optical lithographic processing.

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Semiconductor nanocrystals have garnered much interest recently for potential applications ranging from active media in lasers to biological tagging. While some of this potential has been realized in the case of biological labeling, their use in optical applications, however, has been hindered by the inability to integrate these nanocrystals with standard optical lithography techniques. We present the first results of incorporating these quantum dots within fluorinated polymers that form low-loss waveguides in the near IR and are amenable to optical lithography. Engineering the surface of the quantum dots with suitable surfactants is shown to be critical in stabilizing these nanocrystals in low-loss polymers. Subsequent patterning of these polymers using optical lithographic techniques is demonstrated with the construction of ridge waveguides with low surface roughness. We also construct multi-color layered waveguide structures that could be useful for highly parallel multiplexing applications. By careful choice of the size as well as the composition of the nanocrystals we are able to create waveguides that are luminescent in the visible as well as the IR regions of the optical spectrum. Optical, linear and non-linear, characteristics of these hybrid nanocrystals/polymer waveguides are also presented.