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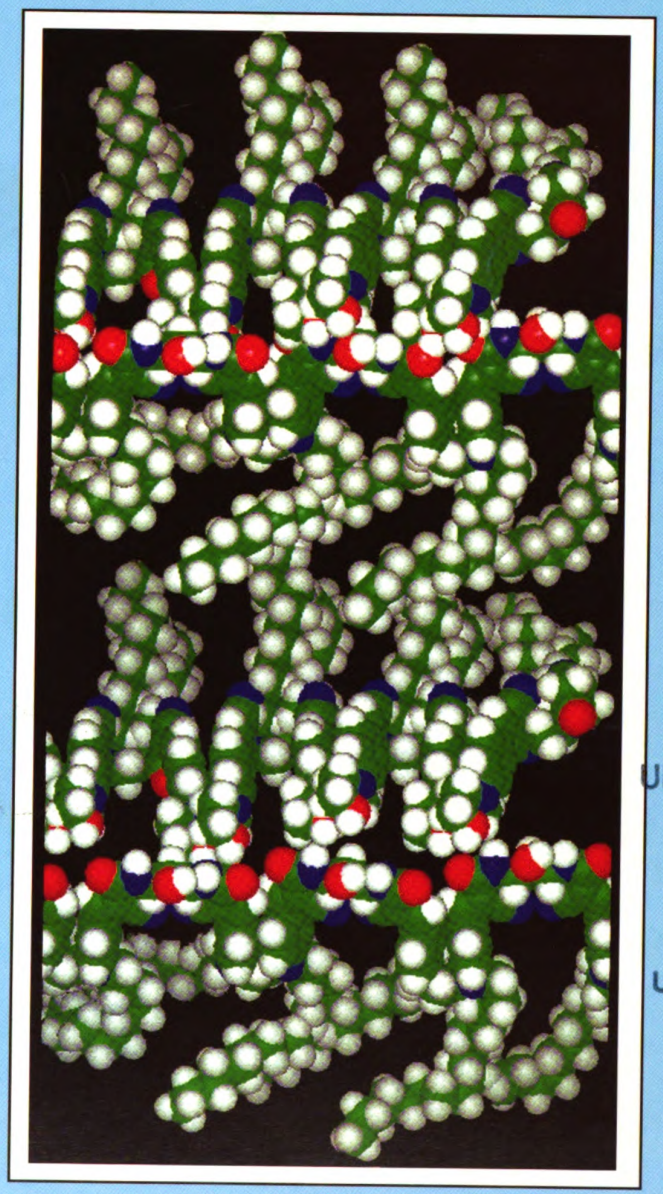

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Photonic and Optoelectronic Polymers

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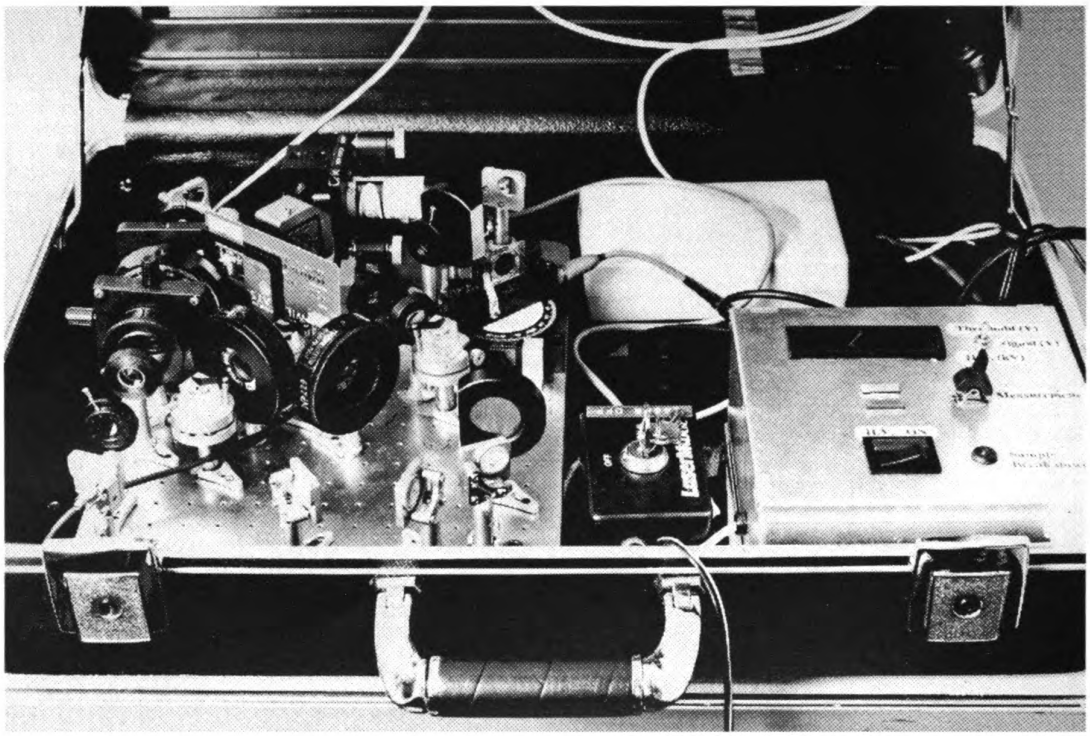

Photograph of a compact polymeric optical reader for credit card security check. A photorefrative polymer is used to implement optical correlation between the optical code on the credit card and the master. (Courtesy of N. Peyghambarian and B. Kippelen, University of Arizona.)

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About the cover

This figure is a 3D computer-graphic representation of the cross-section of an $(AB)_2$ film [four repeat units in each polymer chain: blue = nitrogen, red = oxygen]. **See Article on page 21.**

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Foreword

by Kenneth J. Wynne, Guest Editor
Program Officer, Organic and Polymeric Materials,
Office of Naval Research

This issue of *Naval Research Reviews* contains selected highlights of research supported by the Office of Naval Research (ONR) Polymer Program, focusing on polymers for photonic and optoelectronic applications such as modulators, light emitting diodes, and lasers.

* *Polymers* are "giant molecules". In terms of shape, polymers are the molecular equivalent of angel hair spaghetti or rice noodles. When a polymer is placed in some "solvent" (like noodles in hot water), the material becomes processable (as noodles become soft). Separating the polymer from the processing medium yields a solid mass due to entanglement and in some cases ordering of molecular chains (just like cooked noodles after refrigeration create a solid mass). Economic and environmental considerations require processing most polymers by melting and forming into desired shapes followed by solidification by cooling. Typical melt processed polymers are polyethylene (shopping bags), polypropylene (rope), and polyethylene terephthalate (soda bottles). Today, economical raw material cost (crude oil), easy synthesis, low temperature processing, and an incredible variety of useful products are among the drivers of the multi-trillion dollar polymeric materials industry world wide.

* *Photonics* deals with the use of light (instead of electrons) for information processing. Optoelectronics concerns the utilization of electric fields to generate, modulate, or otherwise influence the behavior of light. Photonic devices are important in the communications field: the use of laser diodes to interrogate our CD's and bring us beautiful music; the use of wide bandwidth optical fibers for carrying millions of telephone conversations with perfect clarity and definition for each pair of conversants.

The reason for this issue on *photonic polymers* is to note some remarkable progress which demonstrates that economical, easily processed "plastics" have growing importance in photonic applications. It is only recently that concepts such as *"polymer modulators"* have been addressed, and only in the last year that the concept of electrically pumped *"polymer lasers"* has been pondered.[1] In this preface, the relevance of this work to our naval forces is presented and background is given on scientific events which led to some of these accomplishments.

Ultrafast information sensing, transmission, processing, and display are of keen interest to naval forces because decision making is based on gathering, processing, and display of data. Recent advances in photonic polymers are thus important because of the great potential for improving command, control, communications, and computers (C4) functions in the battle environment. Some recent discoveries relevant to a broad range of naval applications include: (1) High bandwidth polymer-based electro-optic modulators which convert optical signals to electronic ones, or vice versa, (2) Bright, full color, polymer light-emitting diodes for displays, (3) High diffraction efficiency photorefractive polymers for memory or coding functions, (4) High efficiency polymer photodetectors for visible-UV radiation, (5) Organic thin film transistors comparable to amorphous silicon devices, (6) Tough, thermally stable, high data rate, low-loss polymer optical fibers for light-information transmission which, unlike copper, are impervious to electromagnetic interference and (7) "smart polymers" which, for example, can be rapidly and reversibly converted from one electronic state (which absorbs at a desired wavelength) to another (which reflects). These advances promise more efficient, effective, and economic operations in the C4 area as well as in other areas such as sensing, detection, and camouflage.

Polymeric materials currently play a critical "passive" role in solid state device fabrication as resists, dielectrics, and packaging, but the *active* materials utilized in sensors, cables, modulators, etc., are generally inorganic in nature (Si, SiO_2, ZnSe, etc.). Important exceptions to the usual "passive" role of polymers include the use of photoconductive polymers such as poly(vinyl carbazole) in xerography (Kodak) and the use of piezoelectric polymers such as poly(vinylidene fluoride) (PVDF), in thermal or acoustic sensing. In this regard, a copolymer containing about 20% trifluoroethylene (TFE) and 80% vinylidene fluoride repeat units was synthesized and characterized under ONR Polymer Program support in the mid-seventies at Pennwalt (now AMP) Corporation. Unlike PVDF homopolymer, the new PVDF/TFE copolymer was found to crystallize directly in the piezoelectrically active phase, obviating the need for stretch orientation. This PVDF/TFE copolymer has transitioned to Naval use, for example in acoustic sensing devices in the SSBN 688 class submarines.

Historically, the current ONR Polymer Program emphasis on photonic polymers can be traced back to the mid seventies, and even to a single event. In 1975, when Professor Alan MacDiarmid of the University of Pennsylvania returned from a lecture tour in Japan he called and described an unusual polymer film which he observed in the laboratory of Dr. Hideki Shirakawa, then at the Tokyo Institute of Technology, Laboratory for Resource Utilization in Yokohama. Professor MacDiarmid said the film "was shiny. It looked like aluminum foil." The shiny film was poly(acetylene). The Polymer Program provided some funding to bring Dr. Shirakawa to the University of Pennsylva-

[1]Lasers comprised of dyes dissolved in polymer matrices have been under development since the early 1980's, but ther term "polymer lasers" is meant to mean that the chromophore is part of hte polymer, e.g., as a side chain or part of the main chain.

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nia and soon thereafter chemical and electrochemical "doping" of poly(acetylene) was discovered which led to compositions with extraordinarily high electronic conductivities, as measured in the laboratory of Professor Alan Heeger, also at the University of Pennsylvania at that time. The MacDiarmid, Heeger, Shirakawa collaboration led to a landmark paper and the establishment of the field of intrinsically conducting polymers (ICPs).[2] While a few papers existed on ICPs prior to this work, the insight, enthusiasm, and inquisitiveness of MacDiarmid (a chemist) and Heeger (a physicist) gave rise to an interdisciplinary collaboration necessary for progress. This work led to the discovery of the first polymeric materials which could store electrical energy and deliver charge at a high rate; thus, rechargeable polymer batteries were born. Some recent work from the MacDiarmid laboratory is summarized in the article on page 6. It is seen that ICPs have considerable potential as transparent electrodes for displays and in sensor applications as well.

Interdisciplinary collaboration of chemists, physicists, and materials scientists proved crucial in the later development of *processable* ICPs (fibers, films). In the eighties, the recognition of the importance of the delocalized-electronic state led chemists to the synthesis of new classes of ICPs with improved properties. The chemistry was new because prior to this time chemists had focussed largely on "saturated" chain structures, influenced by the vast majority of commodity polymers, e.g., polyesters and polyolefins such as polyethylene. Unlike polyesters and polyolefins, the unsaturated nature of the main chain makes ICPs less soluble in typical processing media as does the fact that most electronically conducting polymers are salt-like, that is, the polymer backbone is positively charged (polycation) and is associated with discreet counter anions. But the synthesis of new classes of ICPs which were processable, e.g. poly(anilines) and poly(alkoxythiophenes), revealed remarkable and unexpected optical and opto-electronic properties. Thus, in the nineties, research interest has continued on ICPs, but has expanded to embrace the broadening potential of photonic applications. This has happened because the presence of the delocalized electronic state gives rise to potentially useful optical phenomena such as the generation of light by the passage of an electrical current

As an example of exciting new optical phenomena, the article on page 12 by Professor Heeger, describes stimulated emission from poly(alkoxyphenylene vinylenes) which opens an entirely new potential application for polymers with delocalized electronic states: polymer lasers. The results described by Heeger are very new and the promise of economical polymer lasers with emission in the visible and UV spectral regions is tantalizing and potentially of great importance to our armed forces as well as to our economic national competitiveness.

Considering important advances such as the development of photoconducting polymers for use in xerography noted above, utilization of polymers in "active" roles as photonic materials is not without precedent. One might ask though, "why polymers" for high-tech photonic applications, considering the much longer established efforts in traditional inorganic solid state chemistry and physics. The driving forces for the utilization of polymers stem from both economic and technical considerations. The ubiquitous use of polymers in commodity items attests to the economics with ease of processing being key. In device applications, uniform polymer thin films are formed in seconds by placing a polymer solution in the center of a spinning substrate such as glass or silicon. From such a film, hundreds of photonic device structures may be generated by the same microlithographic processes used for solid state electronic circuitry. However, easy fabrication is not alone a sufficient driving force to employ polymers for photonic and optoelectronic applications. Polymeric optical materials and devices must be shown to perform better or to perform functions which are impossible for their inorganic counterparts. Examples of recently discovered "better" and/or "unique" performance include: (1) Higher performance photorefractives (discussed below); (2) Lightweight lenses such as those developed by Donnelly Corporation in Tucson, AZ; they save weight and cost (vs. inorganic glass) and provide high quality optics for camcorder applications by molding PMMA lenses with a corrective micron-scale pattern on the surface, and (3) A *domain inverted structure* for a second order nonlinear optical material which is virtually impossible for an inorganic material such as lithium niobate. Inversion of the polar structure is easily obtained with polar polymers and is the basis for a highly efficient, polarization independent, linear waveguide modulators being developed by Radiant Research, Inc. of Austin, Texas. Other considerations may drive choosing polymers for a particular application, including elimination of the use of heavy metals, for example the use of ICP (carbon) based batteries vs. Cadmium or Lead or concern about availability or cost of scarce elements such as indium.

The potential advantages of photonic polymers may be further understood again using the example of electro-optic modulators. Such devices require a material with a polar (non-centrosymmetric) bulk structure. In inorganic materials, such structures are rare, but lithium niobate is one of the few polar materials and is used for optical modulators. The labor intensive crystal growing, cutting, and fabrication of lithium niobate into solid state devices makes the cost of

[2]*Intrinsically* conducted polymers (ICPs) conduct electricity through a conduction band involving the delocalized electronic state of the backbone of the polymer. Another class of conducting polymers results from the incorporation of a conducting filler such as carbon black or aluminum pieces in an otherwise nonconducting polymer matrix such as polyethylene.

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each device high. Thus, the work on polymer nonlinear optical (NLO) films described by Lindsay (in the article on page 21) is significant in offering the promise of economical, *intrinsically* polar polymer thin films for modulator applications. One can imagine processing hundreds of such modulators from a single thin film on a silicon wafer. Furthermore, for ultrahigh bandwidth application (>100GHz) polymer modulators may be the only choice, as the molecular nonlinearity is electronic rather than lattice-based as for inorganic crystals like lithium niobate.

Another facet to the "why polymers" question can be pursued at this point: "where is industry?" The commodity polymer industry is ill-positioned to do work in the photonic polymer area for a number of reasons. The commodity polymer industry is largely aimed at multi-ton-per-day synthesis of polyolefins and polyesters which are useless as photonic materials (exceptions: poly(methyl methacrylate) and poly(carbonates)). Secondly, teams which develop new products such as a new color line of rubber duckies,[3] lawn mower decks, or even somewhat more challenging reaction injection molded automobile bumpers are poorly positioned for the development of optical materials and devices. Development of the latter demands a *combination* of detailed knowledge of optical physics and polymeric materials and conceptual innovation which is absent in the commodity polymer industry and uncommon even in the best of circumstances elsewhere. The electronics industry is equally poorly prepared to work on photonic polymers, as the bulk of R&D funding is focussed on inorganic solid state materials. As noted above, polymeric materials are largely known to this industry in passive roles such as lithographic resists, dielectric interlayers, and packaging. Furthermore, massive cutbacks in research and development at laboratories which at one time were poised to make important advances (Bell Labs, GTE, aerospace industry) has largely eliminated the long range industrial research efforts required for future innovation in non-traditional areas such as photonic polymers.

In an interesting twist, a fortuitous marriage of private capital and Government SBIR (Small Business Innovative Research) funding has in some measure filled the R&D gap and maintained in our country some momentum and international competitiveness in photonic polymers. Mention has already been made of an Air Force supported SBIR effort at Radiant Research on domain inverted second order nonlinear optical polymer modulators. In the context of this preface some of the efforts currently supported by the ONR Polymer Program and the ONR SBIR program office are summarized. *UNIAX Corporation* of Santa Barbara, CA, is developing thin film polymer light emitting diodes (PLED's) aimed at advanced display capabilities for Department of Defense, and has independently developed economical infrared (IR) polarizing films which can replace expensive copper grids. In a pioneering commercial venture, *Lightwave Microsystems*, Inc., utilizing ONR and other SBIR funding along with their own capitalization has the goal of fabricating economical modulators from state-of-the-art poled polymer films. Such development would have great impact in the development of an important niche market for photonic polymers. This work promises transition to military hardware systems such as phased array radar which requires high bandwidth, low loss transmission, and processing of information acquired by sensors.

Molecular Technologies of Westford, Massachusetts, is developing a new processing approach to polymer optical fibers (POFs). Such fibers would be mechanically and environmentally robust in contrast to glass fibers currently in use. Polymer compositions are targeted to ensure complete transparency at important communication wavelengths. This work follows in the footsteps of the pioneering Japanese scientist Professor Yasuhiro Koike at Keio University in Yokohama. Professor Koike's brilliant work in creating "gradient" refractive index polymeric materials for light guiding is not clearly appreciated in this country. Over the last decade his group has effected exquisite spatial control of the refractive index in polymeric solids in such a way that the lower index material "guides" light in the higher refractive index phase thus, for example routing light in a desired path or changing the focus of light in a desired fashion. The result has been graded index polymeric materials for applications such as lenses for high diopter correction and POF amplifiers through incorporation of rare earth elements in the polymer composition. By generating a parabolic index gradient, a high bandwidth POF was fabricated which allowed multimode signal transmission at 2 GHz.

Kent Display Systems (K'S) of Kent, Ohio, is pursuing work to replace the transparent conductor indium tin oxide

[3]I am obviously being too hard on our important bulk polymers industry which, it should be remembered, together with our chemicals industry is responsible for tens of billions of dollars in a *positive* contribution to our balance of payments. So let me (at the suggestion of Professor Sukant Tripathy) call the readers to an exception to the rule that our commodity polymers people are inactive in high tech photonic polymers. The exception is Mattel Company's "mermaids" which are plastic bathtub toys. These "photonic" plastic toys contain a thermochromic dye which changes color when immersed in warm water thus enlivening the bathtub scene for young bathers. The use of "photonic" polymers in toys reminds me of the first application of "cold light" or chemiluminescence (*Naval Research Reviews* Vol. XXXVI, 1984). A naval research effort which included ONR, Navy laboratory (particularly China Lake), industry, and academic scientists was looking for easily stored emergency lighting. This successful program developed "light sticks" commercialized by American Cyanamid and used by our naval forces in applications such as lighting lines in the night time ship-to-ship transfers and in individual emergency packs in the event of search and rescue. However, the toy industry was a big winner here as can be noted by "glowing necklaces" and other toys at parades or at the beach. All these toys use organic peroxide-based photochemistry developed by the Navy team.

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(ITO) with transparent ICP films for driving liquid crystal displays. The goal here is to make flat panel displays lighter and much more rugged by driving the liquid crystal layer with ICP films on plastic, thereby replacing brittle ITO electrode films on breakable glass. This work has important potential to Navy in providing entirely new concepts for logistics, such as a clipboard-sized, flat panel display which functions as a repair manual with replaceable information chips. The latest scientific and technical information concerning the use of transparent electronically conducing polymers to drive liquid crystalline displays is summarized in the article on page 27, which is a joint contribution from groups at Naval Research Laboratories (NRL) under the direction of Dr. R. Shashidhar and Kent State University under the direction of Professors William Doane (now Emeritus) and William Fritz.

Directing the ONR Polymer Program research effort over many years has been exciting and challenging because of the "surprises", that is, unanticipated turns in the paths of research which have led to lush new valleys of opportunities. One of these surprises is described in the article on page 31 which summarizes a research thrust directed by Professors Sukant Tripathy and Jayant Kumar at the University of Massachusetts, Lowell. This work describes an unusual photophysical effect which leads to the production of precise surface gratings and other regular structures simply by shining a light pattern on the surfaces of polymer films containing the azobenzene chromophore. This phenomenon is very new and entirely unexpected and is associated with the "pumped" trans-cis-trans isomerization of the azo chromophore. The production of precise gratings promises economical, high efficiency coupling and diffraction devices for applications in wave guides, modulators, and polymer optical fibers.

The success of work in photonic polymers led to the initiation of two Multidisciplinary University Research Initiatives in 1995, one at the University of Arizona under the direction of Professor Nasser Peyghambarian and the other at the University of Massachusetts, Lowell under the direction of Professor Sukant Tripathy. An exciting highlight of the Arizona MURI research is summarized in the article on page 40 which describes the emergence of photorefractive polymer compositions which have exceeded the performance of inorganic crystals such as lithium niobate. The high level of performance which has been developed in a very short time makes photorefractive polymers important candidates for new technology in the areas such as dynamic holographic testing and optical information processing. Naval interest in this area is clearly demonstrated in the all-optical pattern recognition system for security verification described in this chapter.

The highlights selected for this issue of *Naval Research Reviews* summarize important research progress which will impact naval forces by providing improved materials and devices for C4, stealth, sensors and detection, and in other areas which our imaginations at this time cannot perceive. Unfortunately, many other exciting research thrusts could not be included in this volume because of space limitations. The selected highlights should convey how rapidly the field of photonic and optoelectronic polymers is evolving and the important impact of this progress to the strategic and tactical readiness of our naval forces.

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Application of Thin Films of Conducting Polymers in Microcontact-Printed Liquid Crystal Displays

Alan G. MacDiarmid
Department of Chemistry, University of Pennsylvania

Introduction

The ability to cast high quality thin films of conducting polymers from their solutions in organic solvents (1,2) or to deposit them on selected substrates from aqueous solutions (3-5) has permitted their use both in their lowly conducting (6) and also in their highly conducting forms (7) in novel devices. The non-doped semiconducting form of polyaniline (emeraldine base; EB) can, for example, be conveniently spin-case from its solution in N-methypyrrolidinone (NMP) to produce high quality thin films (4,5). Thin cohesive films of polyaniline (4,5) and polypyrrole (3,4) in their doped, highly conducting form can readily be deposited on selected polymer or glass substrates by a "1-dip" in situ process from dilute aqueous solutions of the monomer where it is undergoing oxidative polymerization.

Additionally, recent studies on the microcontant printing (μCP) technique (8) shows that hydrophobic patterns with micron dimensions can be formed on hydrophilic surfaces without involving photolithographic-type procedures. This suggests a convenient approach for making patterned thin films of conducting polymers on a micron scale by combining the "1-dip" in situ process (4,5,9) for depositing polypyrrole and polyaniline film with certain μCP techniques (e.g., wax engraving) which uses only common laboratory equipment.

In this paper, we describe the selective deposition of films of polyaniline and polypyrrole on $C_{18}H_{37}$-patterned hydrophilic glass surfaces and their use in novel electroluminescent and liquid crystal display devices and in "microcontact printing".

"1-Dip" in situ Deposition of Polypyrrole and Polyaniline on Hydrophobic and Hydrophilic Glass Surfaces

High quality thin films of doped polypyrrole and doped polyaniline can be conveniently deposited during a few minutes at room temperature on glass and plastic substrates from dilute aqueous solutions of the respective monomer as it undergoes oxidative polymerization (3-5,10). We find that the deposition rate and the properties of the films are greatly dependent on the nature of the substrate surface, e.g., whether deposited on hydrophilic or hydrophobic surfaces.

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Glass microscope slides may be readily rendered hydrophilic (advancing water contact angle <~5°) by treatment with a hot concentrated sulfuric acid/30% hydrogen peroxide mixture or hydrophobic (advancing water contact angle ~110°) by a standard treatment involving exposure to ~0.4 wt% hexane solution of $C_{18}H_{37}SiCl_3$.

Figures 1 and 2 show the result of deposition studies involving polypyrrole (10) and polyaniline respectively in which treated glass microscope slides were dipped in the same solution of polymerizing monomer for the same length of time. In both cases, the rate of deposition of polymer on the hydrophobic surface is very much greater than on the hydrophilic surface. We believe that this may be related to the "like dissolves like" principle, i.e., some of the covalent monomer is preferentially adsorbed from the aqueous solution on to the covalent $C_{18}H_{37}$- film coating the surface more so than on to the polar hydrophilic glass surface, thus favoring more rapid polymerization on the hydrophobic surface. For both polymers, adhesion is stronger to the hydrophilic surface, the films passing the "Scotch Tape" test.

Figure 1
Vis/uv spectra of polypyrrole anthraquinone-2-sulfonate deposited (dipping time: 15 minutes) on (A) a hydrophobic glass surface (film thickness ~400Å) and (B) a hydrophilic glass surface. (Spectrum A was recorded vs. a hydrophobic glass slide in the spectrometer reference beam and spectrum B was recorded vs. a hydrophilic glass slide in a spectrometer reference beam).

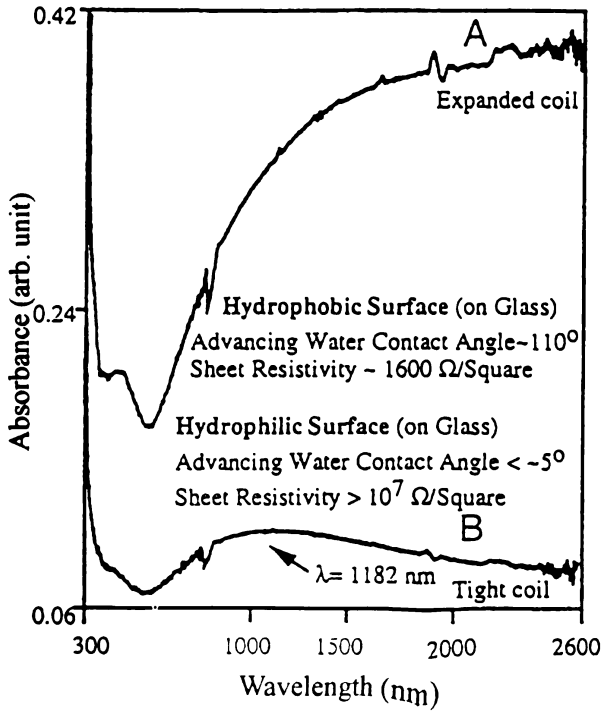
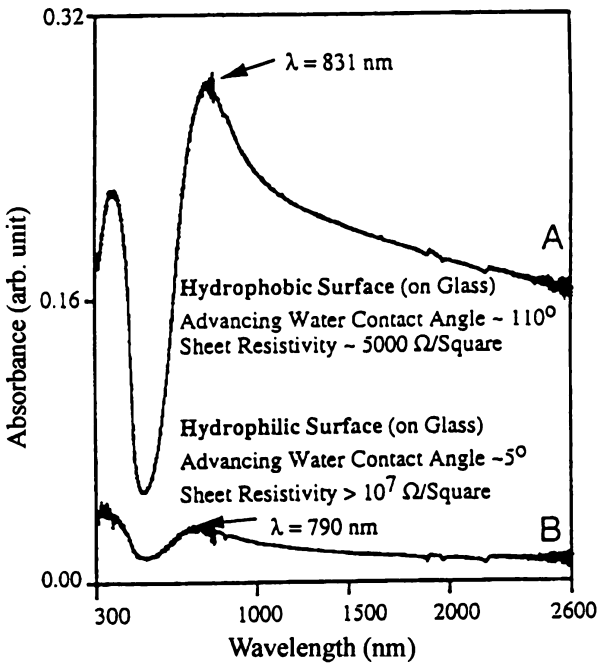


Figure 2
Vis/uv spectra of polyaniline.HCl deposited (dipping time: 5.5 minutes) on (A) a hydrophobic glass surface (film thickness ~1200Å) and (B) a hydrophilic glass surface. (Both spectra were recorded vs. "as-received" glass microscope slides in the spectrometer reference beam).



Not surprisingly, the surface resistance of the thinner films on the hydrophilic surfaces is very much greater than that of the thicker films deposited on the hydrophobic surfaces. It is also possible that the conductivity of the films deposited on the hydrophilic and hydrophobic surfaces may differ from each other. This possibility is presently being investigated.

As can be seen from Figure 1, the spectra of the polypyrrole films deposited on hydrophilic and hydrophobic surfaces differ greatly, the peak at 1182 nm for example in the former spectrum being absent in the latter spectrum which instead shows a well defined free carrier tail extending to 2600 nm. By analogy with studies on polyaniline (11), we believe that the polymer deposited on the hydrophilic surface might have a tight coil molecular conformation while that deposited on the hydrophobic surface might have an expanded coil molecular conformation.

It can be seen from Figure 2 that the spectra of the polyaniline films differ, although not as greatly as for the polypyrrole films, according to whether the polyaniline is deposited on hydrophilic or hydrophobic surfaces. It should be noted that different dopant anions were used for the polypyrrole and polyaniline films. On-going studies suggest that the two polymers may behave even more similarly when they both have the same dopant anion. For both

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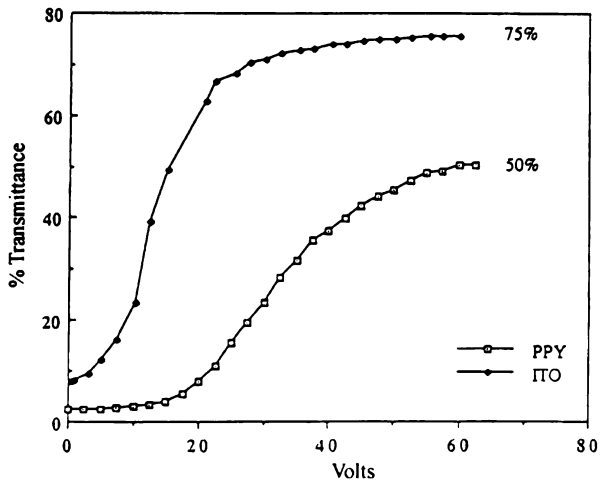
polyaniline and polypyrrole thin films, the sheet resistivity of the films on the hydrophilic surfaces is at least 3 orders of magnitude greater than that of the films deposited on the hydrophobic surfaces.

Flexible Liquid Crystal "Light Valves"

Novel, flexible, completely organic, polymer dispersed liquid crystal (PDLC) "light valves" were fabricated using two flat pieces of commercial overhead transparency substrates (Nashua *xf*-20) coated with polypyrrole between which a film of commercial PDLC material (Norland Products Co. NOA 65 optical adhesive and spacers) was sandwiched. The optical adhesive was polymerized by exposure to UV light. Thin conducting polypyrrole films of varying controllable thickness were deposited on the overhead transparency.

For use in flat screen liquid crystal displays it is necessary to optimize the thickness of the polypyrrole deposit so as to simultaneously obtain the maximum transmittance and minimum resistance necessary for satisfactory devices. For example, a 10 minute dip of Nashua *xf*-20 overhead transparency produces a polypyrrole film having a thickness of ~250 angstroms, a surface resistivity of 7,200 ohms/square and a transmittance centered near the middle (600 nm) of the visible region (~400 nm to ~800 nm) of 89% using an uncoated substrate in the reference beam of the spectrometer. Figure 3 illustrates preliminary results obtained to date with a completely flexible, all organic light valve using polypyrrole as the conducting medium for both electrodes (12). A PDLC device using conducting ITO glass for both electrodes was used as a standard for comparison. The results are satisfactory for certain applications such as lightweight, non-breakable windows of variable transmittance.

Figure 3
Relationship between transparency (% transmittance in air at 600nm) and applied voltage of polymer dispersed liquid crystal display devices constructed using two ITO glass electrodes and two polypyrrole film (on plastic) electrodes as the conducting transparent substrates.



Application of "Microcontact Printing" for the Production of Patterned Polypyrrole and Polyaniline Films

We are combining the selective deposition of polypyrrole and polyaniline on hydrophilic/hydrophobic surfaces as described in the preceding section with the recent microcontact printing technique (8, 13-15) to produce patterned conducting polymer films which we have demonstrated can be used in PDLC display-type devices.

A key objective of the collaborative research with G. M. Whitesides and Y. Xia (Harvard University) is to determine the maximum resolution of polyaniline and polypyrrole patterns attainable using only simple, commonly available equipment, i.e., a desktop computer and a standard spectrometer plotter, (resolution ~25um). The steps comprise: (i) designing any desired pattern on the computer; (ii) reducing the pattern on the computer to any desired size, e.g. >~1 cm x 1 cm; (iii) transferring the design to a floppy disk; (iv) inserting the disk into the computer driving the plotter of the spectrometer; (v) replacing the pen in the plotter by an object with a sharp point, e.g., a sewing needle; (vi) covering, e.g., by spinning or other means, a heated microscope slide or silicon wafer with a thin layer (~ 20-40 um) of low melting (working temperature ~52°) wax such as Amaco Flexwax 120; (vii) scratching the pattern on the thin layer of wax using the needle in the pen holder of the plotter, and placing it (attached to is substrate) in a petri dish; (viii) pouring a well stirred mixture of Dow Corning Sylgard 184 silicone elastomer (10 parts by weight) and Sylgard 184 curing agent (1 part by weight) on top of the wax engraving to a depth of 5-10 mm; (ix) allowing the mixture to polymerize to the silicone elastomer during ~ 3 days at room temperature; (x) removing the silicone stamp from the wax-engraved pattern and discarding (it has the wax "scrapings" produced in the engraving of the pattern adhering to it); (xi) repeating step (viii) and allowing polymerization; (xii) removing the silicone elastomeric stamp which now has the 3-D design imprinted on its lower face; (xiii) wiping the patterned face of the silicone stamp with a piece of cotton containing the "ink" as a ~0.4 wt% solution of $C_{18}H_{37}SiCl_3$ in n-hexane; (xiv) evaporating the n-hexane in a stream of nitrogen for ~1 minute; (xv) pressing the stamp firmly for ~10 seconds on

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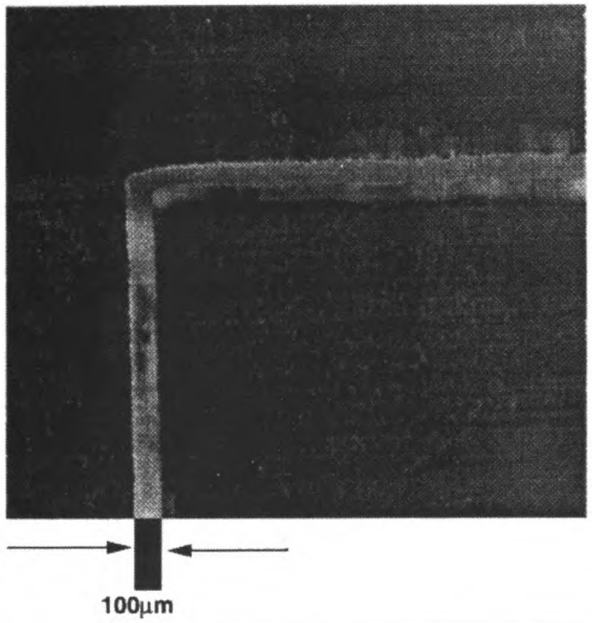
Figure 4
SEM of polyaniline.HCl selectively deposited by a "1-dip" process on a ~100μm wide line of hydrophobic $C_{18}H_{37}SiCl_3$ substrate.

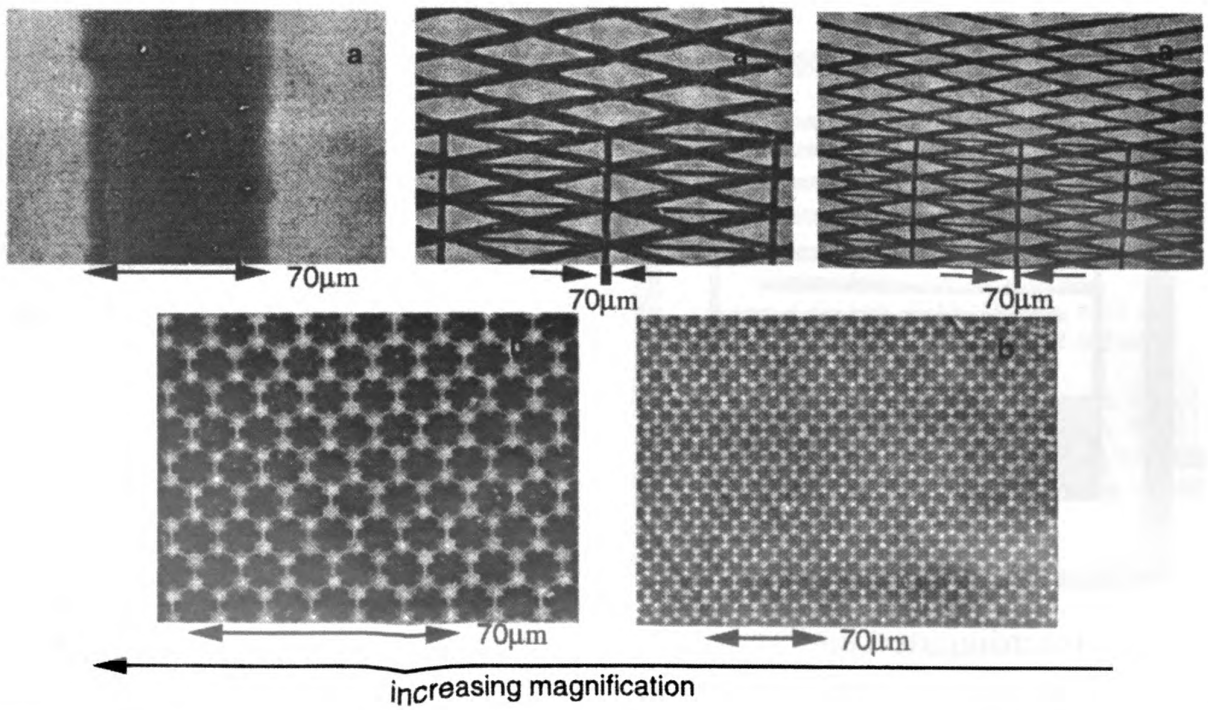


the substrate surface so as to imprint a pattern of a thin hydrophobic $C_{18}H_{37}$ -film on the substrate; (xvi) immediately cleaning the stamp by rinsing it with cotton soaked in n-hexane; (xvii) placing the substrate with the imprinted $C_{18}H_{37}$ -layer in to the appropriate dipping solution.

An example of an SEM of polyaniline. HCl selectively in situ-deposited (5.5 minute dipping time) on an ~100 um wide hydrophobic $C_{18}H_{37}$ -line imprinted on a clean, hydrophilic microscope slide is given in Figure 4.

Examples of the selectivity of polypyrrole 1-dip, in situ, deposition are given in the SEMs in Figure 5. Dark lines are polypyrrole selectively deposited on hydrophobic $C_{18}H_{37}$ -surfaces imprinted on a clean, hydrophilic microscope slide as substrate. The upper three figures (Figures 5a) originated from a desktop computer-drawn pattern used for producing the wax engraved master; the deposition time in the polymerizing pyrrole solution was 12.0 minutes' Preliminary studies directed towards optimizing both the selectivity of deposition and resolution using the wax engraving technique are very encouraging. The lower two figures (Figures 5b) demonstrate the resolution attainable using a commercial relief master from which the silicone stamp was made. Our objective is to attain these types of results using the (non-lithographic) wax engraving technique. Since the silicone stamps can be used repeatedly without loss of reso-

Figure 5
Selective deposition of polypyrrole on patterned hydrophobic surface.



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lution (13,14), this technique holds potential promise for the inexpensive production of semi-micro circuitry and liquid crystal displays on rigid or flexible substrates in certain types of "throw away" devices such as, e.g., sensors.

As an example, an effective polymer dispersed liquid crystal interdigitated array display has been fabricated by combining the concepts and techniques given in the "Flexible Liquid Crystal Light Valves" section with those given in this section. A thin interdigitated polypyrrole display pattern was deposited on a glass microscope slide as described above from the computer designed pattern given in Figure 6. Its thickness was chosen so that its optical transmittance and surface resistance were appropriate for liquid crystal display purposes. The PDLC mixture was sandwiched between the microscope slide (the polypyrrole pattern acting as one electrode) and ITO coated glass which acted as the other electrode. When placed on an overhead projector, the whole device produced a dark image on the screen. As shown in Figure 7, application of an AC potential to the ITO/glass electrodes and one half of the pattern, produced a clear bright image of that half of the pattern, strong light passing through the semi-transparent polypyrrole line electrodes. Application of the potential to both polypyrrole electrodes resulted in both halves of the interdigitated polypyrrole array appearing as a white pattern on a black background on the projector screen. This dramatically demonstrates the large difference in surface resistance between polypyrrole deposited on hydrophobic vs. hydrophilic surfaces as described in Figure 1.

Conclusions

It is concluded that thin films of conducting polymers such as polyaniline and polypyrrole, whether in their highly or lowly conducting forms, whether cast from their solutions in organic solvents or deposited from solutions of the polymerizing monomer are of both fundamental scientific interest and of possible technological use for certain applications. Polypyrrole thin films formed on hydrophobic glass surfaces differ greatly in thickness and electronic properties from those on hydrophilic glass surfaces. This selectivity has been used in forming patterned polyaniline and polypyrrole thin films on microscope slides, which can be used as electrodes in fabricating liquid display devices, etc. Preliminary studies directed towards optimizing both the selectivity of deposition and resolution using the wax engraving technique are very encouraging. Since silicone stamps can be used repeatedly many times without loss of resolution, this technique holds potential promise for the inexpensive production of, e.g., semi-micro circuitry and liquid crystal displays on rigid or flexible substrates in certain types of "throw away" devices such as, e.g., sensors. However, much still remains to be understood concerning the role of conjugated polymers in various light-emitting devices and the effect on their properties induced by the nature of the substrate surface on which they are deposited.

Figure 6
Computer constructed and computer reduced (17mm x 17mm) interdigitated array.

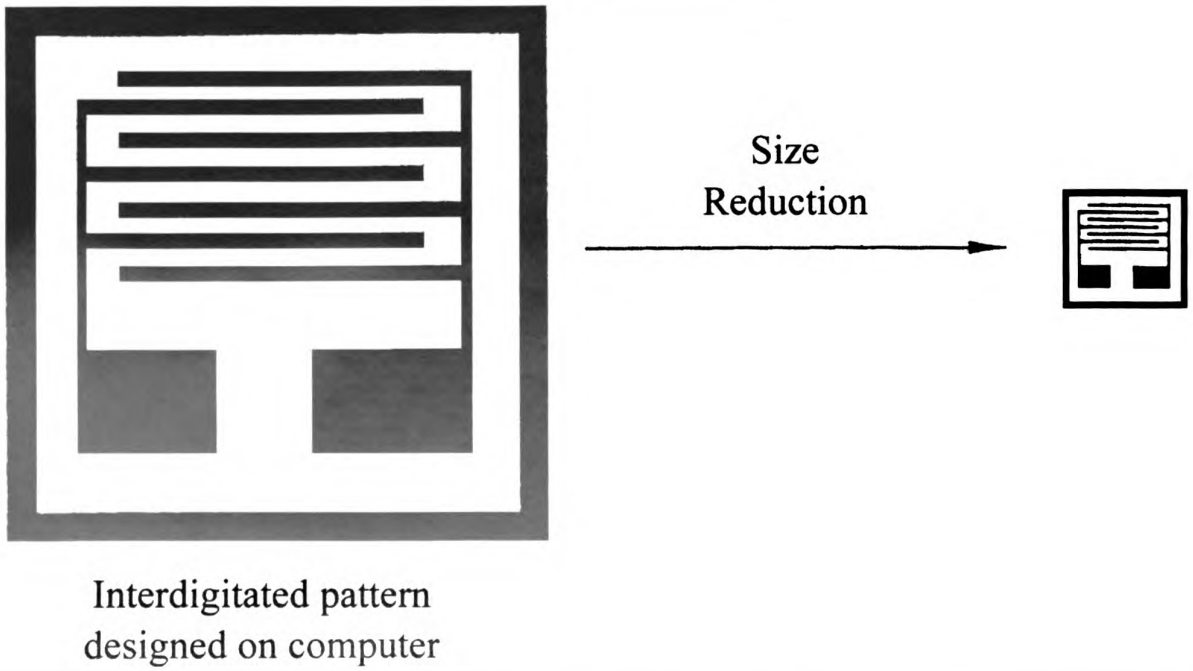

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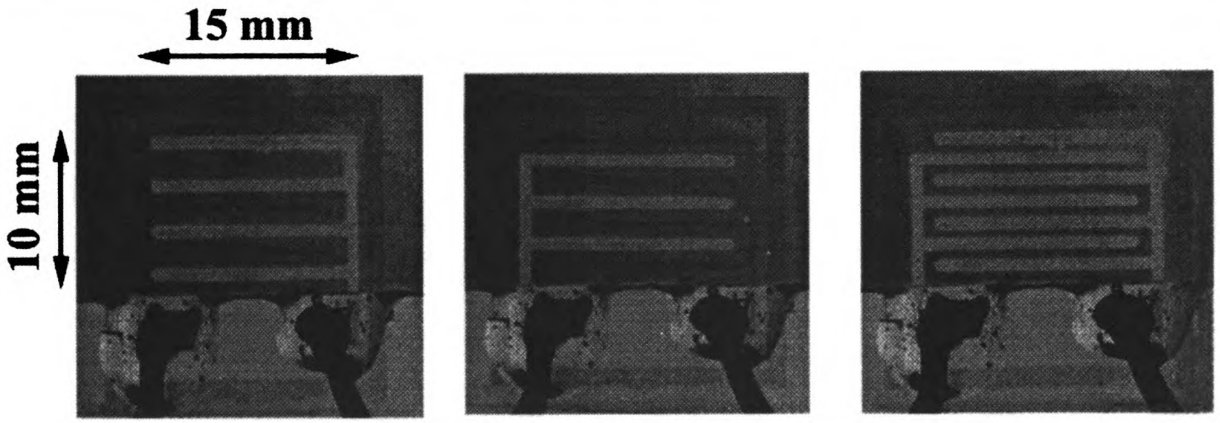
Figure 7
Microcontact-Printed Liquid Crystal (PDLC) Display. Light shines through the thin transparent polypyrrole pattern which also acts as one electrode. Power on: (a) right hand electrode; (b) left hand electrode; (c) both electrodes.



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Biography

See Profiles in Science on page 49.

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Conjugated Polymers as Thin Film Solid-State Laser Materials: Photopumped Gain-Narrowing in Waveguides and Lasing in Microcavities

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Abstract

Optically pumped gain narrowing and lasing have been demonstrated in submicron thick films, neat and undiluted, of photoluminescent conjugated polymers. The dramatic collapse of the emission line width (to as little as 7 nm) occurs at very low pump energy thresholds (< 10 μJ/cm²). Gain narrowing is found in over a dozen different conjugated polymers representing a variety of molecular structures, including poly(*p*-phenylenevinylene), poly(*p*-phenylene) and polyfluorene derivatives; the emission wavelengths in these materials span the visible spectrum. The short gain lengths in conjugated polymers are attributed to the high density of chromophores, the large density of states associated with the interband (π-π*) transition in quasi-one-dimensional systems, and the Stokes shift which minimizes self-absorption and which allows optical pumping to the excited state without simultaneously stimulating emission (thereby yielding population inversion). Lasing and gain narrowing are compared for a soluble poly(*p*-phenylene) derivative using two different resonant structures: planar waveguides and microcavities. In both cases, the gain narrowing threshold is at 0.05 - 0.1 μJ per 10 ns pulse focused to ~1.5 nm. Gain narrowing is not observed in films on indium tin oxide (ITO) substrates unless a cladding layer is placed between the luminescent polymer and ITO. Single-mode microcavity lasers are obtained when a cavity resonance occurs at the wavelength where the gain of the polymer is maximum.

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I. Semiconducting Polymers as Materials for Solid State Lasers

Many conjugated polymers are luminescent materials with emission that is shifted sufficiently far from the absorption edge that self-absorption is minimal. Because of the large joint density of states associated with the direct π to π^* (interband) transition of these quasi-one-dimensional semiconducting polymers, the absorption coefficient (α) is large, typically $\alpha \approx 10^5 cm^{-1}$ or greater.[1] To first order, the cross-section for stimulated emission (SE) is the same as that for absorption, so the gain length should be essentially equal to the absorption length scaled by the fraction of chromophores in the excited state.[2] Therefore, an inverted population can be achieved by pumping the π to π^* transition; this does not simultaneously stimulate emission because the absorption and emission are spectrally separated. Thus, semiconducting luminescent polymers offer promise as novel laser materials with gain lengths in the micron or sub-micron regime.

A variety of optoelectronic devices have been demonstrated using conjugated polymers as the active semiconducting materials, including diodes,[3] light emitting diodes,[4] photodiodes,[5] field-effect transistors,[6] polymer grid triodes,[7] and light emitting electrochemical cells.[8] Notably absent from this list of conjugated polymer devices, however, is the semiconducting polymer injection laser. In the past, laser emission had been observed from poly(2-methoxy, 5-(2'-ethylhexyloxy)-1,4-phenylene vinylene), MEH-PPV, in dilute solution in an appropriate solvent, in direct analogy with conventional dye lasers.[9] Interest in using semiconducting polymers as *solid-state* laser materials was initiated by the recent demonstration of gain narrowing in which the gain material was a dilute blend of MEH-PPV (less than 1 %) in polystyrene[10]; these thick (~100 μm) films contain a dispersion of TiO_2 nanoparticles which confine the emitted photons by multiple scattering so that the distance traveled in the medium exceeds the gain length. Photopumped gain narrowing has now been reported for submicron thick films, neat and undiluted, of over a dozen soluble conjugated polymers, including poly(*p*-phenylenevinylene) (PPV), poly(*p*-phenylene) (PPP) and polyfluorene (PF) derivatives, in planar waveguide structures.[11,12] and lasing has been observed from PPV[13] and from BuEH-PPV(see below and reference 24) in microcavities. New polymers have been developed that also show gain narrowing in solution[14,15] and in the solid state.[16,17]

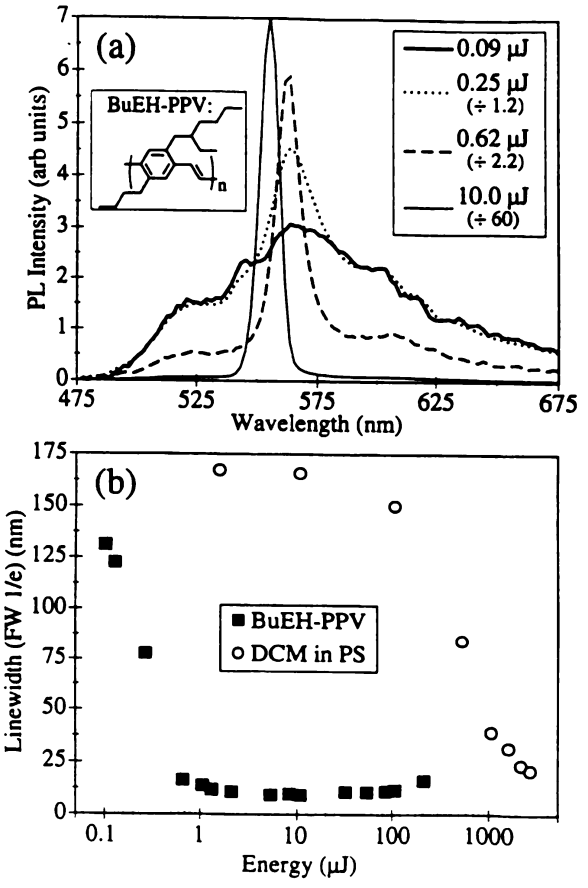
The instrumentation for gain narrowing experiments using thin solid film waveguides has been described in detail elsewhere.[10] Light emission was typically collected from the front face of the sample, but gain narrowed emission could be detected in all directions. The excitation source (the pump) was a 10 Hz, *Q*-switched Nd:YAG laser which provided ~10 ns pulses at 532 and 355 nm focused to ~1.5 mm. The first anti-Stokes Raman line (435 nm) from a high pressure H_2 cell pumped at 532 nm was also used. The energy per pulse was controlled with calibrated neutral density filters.

The PL spectrum evolution for a neat film of BuEH-PPV, 210 nm thick, is shown as a function of the pump energy per pulse in Figure 1a. As the pump energy is increased, a gain-narrowed peak rises out of the broad emission spectrum, until at sufficiently high energies, only the gain-narrowed peak survives while the broad tails of the PL are completely suppressed. This dramatic collapse of the line width[18] (from 130 nm to 9 nm) at remarkably low pump energies (≤

Figure 1

(a) Photoluminescence spectrum of 210 nm thick BuEH-PPV neat film on glass (spin cast from p-xylene solution) at various pump pulse energies both above (10.0 μJ, thin solid curve; 0.62 μJ, dashed curve) and below (0.25 μJ, dotted curve; 0.09 μJ, thick solid curve) the lasing threshold. Inset: Chemical structure of BuEH-PPV.

(b) Evolution of the line width (full width at 1/e height) as a function of pump pulse energy (on a log scale) for the BuEH-PPV sample of (a) (squares), and for comparison, a 2.6% by weight film of DCM laser dye in PS (open circles) of 3600 nm thickness with comparable optical density to the BuEH-PPV film.



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1 μJ per pulse) indicates that these undiluted thin films have a very short gain length. A blue shift of the emission peak at higher energies is also evident in Fig. 1a, which suggests that SE occurs on a time scale faster than the spectral diffusion which occurs during the first few tens of picoseconds (ps) following photoexcitation.[10] Fig. 1b displays the line width of the PL as a function of pump pulse energy, demonstrating a well-defined threshold for gain narrowing.

If the gain lengths are indeed in the micron or submicron regime, the energy threshold for gain narrowing should be much lower than for conventional laser materials. For reference, therefore, we tested the laser dye DCM, (4-dicyanomethylene-2-methyl-6-(*p*-dimethylaminostyryl)-4*H*-pyran), [19] (see Table 1) suspended in films of polystyrene (PS) with optical densities comparable to those of the 210 nm BuEH-PPV film of Fig. 1. Dye molecules like DCM are known to undergo concentration quenching; that is, their quantum yield for luminescence drops dramatically when the dye is present in too high a concentration. Thus, the DCM concentration (2.6 %) in PS was optimized for maximum luminescence. Although the DCM concentration is more than two orders of magnitude higher than in typical dye lasers, the threshold for gain narrowing is over 1000 times higher than that of BuEH-PPV, as shown in Fig. 1b. Thus, conjugated polymers provide the intense absorption and emission characteristics of organic dyes, but with the substantial advantage of having a much higher density of chromophores in the solid-state.

We have explored gain narrowing and lasing from a number of PPV derivatives[20] and from polymers with the PPP and PF backbone structures; the corresponding π-π^* energy gaps span the visible spectrum. The chemical structure, excitation wavelength, peak emission, energy threshold for line narrowing, and narrowed line width for thin films of these various semiconducting polymers are summarized in Table 1. The very low energy thresholds for gain narrowing indicate that semiconducting polymers comprise a class of promising laser materials with emission spectra that span the full range of the visible portion of the spectrum.

The data in Fig. 2 demonstrate the advantages of the high density of chromophores characteristic of semiconducting polymers. The linewidths vs. pump energy of films of varying BCHA-PPV (see Table 1 for complete name) concentration diluted in PS are shown in Fig. 2. Upon increasing the concentration of BCHA-PPV in the film from 8.4 % to 100% (a factor of 12) the threshold energy decreased by three orders of magnitude, to a minimum of 1.3 μJ per pulse for the neat film. This strongly superlinear behavior may be indicative of coherent emission from the BCHA-PPV.[21]

TABLE 1

Material	Peak PL emission (nm)	λ_{pump} (nm)	Energy Threshold (μJ/pulse)	Final Linewidth (nm)	Film Thickness Range (nm)	Cutoff Thicknes (nm)	Solvent
BuEH-PPV[a]	520, 560	435	0.4 ± 0.2	12	126-252	106 ≤ Th ≤ 126	THF
			0.2 ± 0.1	9	87-208	65 ≤ Th ≤ 87	*p*-xylene
BCHA-PPV[b]	540, 630(sh)	532	1.0 ± 0.4	11	277-650	160 ≤ Th ≤ 277	THF
MEH-PPV[c]	585, 625	532	1.1 ± 0.4	17	87-405	53 ≤ Th ≤ 87	THF
			3	50	355	<355	CB
			4	55	325	<325	*p*-xylene
BEH-PPV[d]	580, 650	532	0.5	13	300	<300	THF
MOC10-PPV[e]	530, 620	532	4	16	310	<310	THF
BuEH-MEH Copolymers[f]							
10:90	580, 625	532	3.2	23	330	<330	THF
70:30	565, 600	532	1.0	15	420	<420	THF
90:10	550, 580 (sh)	435	1.0	20	370	<370	THF
95:5	545, 580 (sh)	435	1.6	20	450	<450	THF
97.5:2.5	540, 570 (sh)	435	1.0	18	500	<500	THF
HEH-PF[g]	425, 445	355	4.2	12	120	<120	THF
BDOO-PF[h]	430, 450, 540	355	2.3	7	-	-	THF
CN-PPP[i]	420	355	4	12	100	<100	THF
DCM/PS[j] (2.6% w/v)	640	532	400± 150	23	390-4800	260 ≤ Th ≤ 390	THF

[a]poly(2-butyl-5-(2'-ethylhexyl)-1,4-phenylenevinylene); [b]poly(2,5-bis(cholestanoxy)-1,4-phenylene vinylene),; [c]poly(2-methoxy 5-(2'-ethylhexyloxy)-1,4-phenylenevinylene); [d]poly(2,5-bis(2'-ethylhexyloxy)-1,4-phenylene vinylene); [e]poly(2-methoxy-5-(2,7-dimethyl-octyloxy)-1,4-pheneylenevinylene); [f]copolymers synthesized from varying ratios of BuEH-PPV and MEH-PPV monomers; [g]poly(9-hexyl-9-(2'-ethyl-hexyl)-fluorene-2,7-diyl); [h]poly(9,9-bis(3,6-dioxaoctyl)-fluorene-2,7-diyl); [i]poly(2-(6'-cyano-6'-methyl-heptyloxy)-1,4-phenylene); [j]4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran

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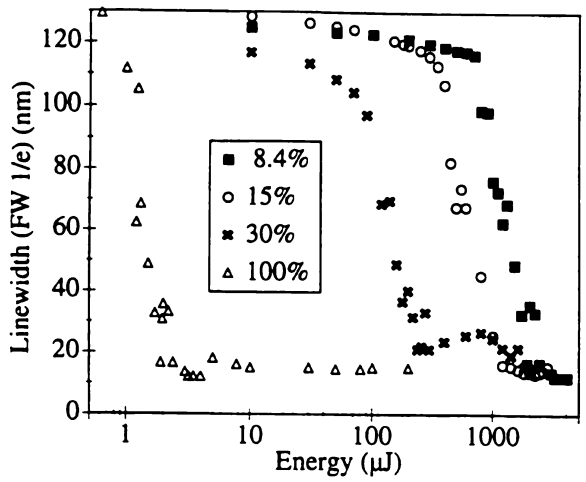
Figure 2
Emission line width as a function of pump pulse energy (on a log scale) for various BCHA-PPV/PS blend films at different BCHA-PPV concentrations: 8.4% (squares), 15% (open circles), 30% (crosses) and neat (100%) (open triangles).



II. Gain Narrowing in Planar Waveguides

Asymmetric planar waveguides formed from the refractive index mismatch at the polymer/air and polymer/substrate interfaces of a thin film provide a straightforward and relatively simple method for extending the path length of the emitted photons in the gain medium. The role of waveguiding in optically pumped polymer films has been carefully documented. The results prove that extension of the optical path by waveguiding plays an important role in the observed gain narrowing behavior in thin film samples of this class of plastic laser materials.

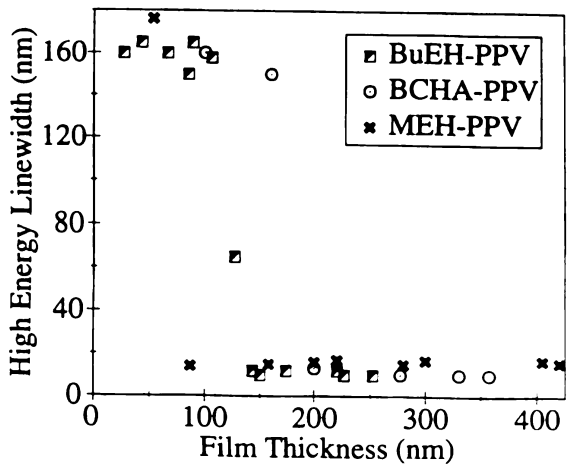
In general, the refractive indices (n) at the emission wavelengths for all the polymers studied are in the range $1.56 \leq n_{polymer} \leq 2.0$; i.e. larger than those of the surrounding media ($n_{glass} = 1.52$, $n_{air} = 1.0$) in thin film samples. Therefore, neat polymer films cast over glass substrates constitute asymmetric planar waveguides: air/neat polymer film/glass. For this type of asymmetric thin film structure, a cutoff film thickness (h_{cutoff}) exists, below which the fundamental mode cannot propagate:[22]

$$h_{cutoff} = \frac{\lambda}{2\pi\sqrt{n_f^2 - n_c^2}} \tan^{-1}\sqrt{\frac{n_s^2 - n_c^2}{n_f^2 - n_s^2}} \qquad (1)$$

where λ is the wavelength of the guided light, and the subscripts c, f, and s refer to cladding, film and substrate respectively. In the present case c = air, f = neat polymeric film, and s = glass. The refractive indices of BuEH-PPV and BCHA-PPV films were determined from modal waveguide characterization at 633 nm.[22] Spin-cast films exhibit birefringence: the refractive index in the plane of the film, determined from the angular position of the TE modes, was n = 1.69 for BuEH-PPV and n = 1.60 for BCHA-PPV, while the refractive index in the direction perpendicular to the plane of the film, determined from the angular position of the TM modes, was measured as n = 1.55 for BuEH-PPV and n = 1.53 for BCHA-PPV (the case of MEH-PPV is discussed below). Using the in-plane values of n in Eq. 1, the calculated h_{cutoff} values are 120 nm and 200 nm for BuEH-PPV and BCHA-PPV films on glass, respectively.

The dependence of gain narrowing on film thickness was studied experimentally for neat films of three conjugated polymers: BuEH-PPV, BCHA-PPV, and MEH-PPV, as well as for the reference films of DCM in PS. The film thicknesses used ranged from 27 to 252 nm for BuEH-PPV, 160 to 650 nm for BCHA-PPV and 52 to 405 nm for MEH-PPV. To demonstrate the effects of thickness on the gain narrowing behavior, we plot the high energy (≥ 10 μJ) PL line width as a function of the film thickness for each of these three polymers in Figure 3. A well defined cutoff thickness for the presence of gain narrowing is evident at 116 ± 10 nm for BuEH-PPV, 215 ± 30 nm for BCHA-PPV and 70 ± 15 nm for MEH-PPV. Thus, for both BuEH-PPV and BCHA-PPV, the experimentally observed cutoff thicknesses are in excellent agreement with the values calculated from the asymmetric waveguide cutoff formula, Eq. 1. The observed cutoff thickness for the DCM/PS films leads to a cal-

Figure 3
Linewidth of the PL spectrum at a high pump energy (≥ 10 μJ per pulse) as a function of the film thickness for BuEH-PPV (half-filled squares; 435 nm excitation), BCHA-PPV (dotted circles; 532 nm excitation) and MEH-PPV (heavy crosses; 532 nm excitation) films spun from THF on glass substrates.



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culated n between 1.56 and 1.59, in excellent agreement with handbook values for the index of refraction of pure PS.

The variation in the experimental cutoff thicknesses with polymer (Fig. 3) arises from differences in the polymer refractive indices. The larger the refractive index of a polymer film, the lower the cutoff film thickness for the observation of gain narrowing. The close correspondence of experimental and calculated cutoff thicknesses for the propagation of the fundamental mode in BCHA-PPV and BuEH-PPV offers a method for determining the refractive index for those materials where waveguide characterization cannot be used. For MEH-PPV, the refractive index of the film was calculated from the cutoff thickness (usin Eq. 1) to be in the range $1.8 \leq n_f \leq 2.0$. This is consistent with the fact that the light could not be coupled into the MEH-PPV film in the modal waveguide characterization experiment since the refractive index of the prism coupler ($n \sim 1.8$) is comparable to or lower than that of the film. This relatively high calculated value of the index for MEH-PPV is also consistent with other reports in the literature.[23]

Additional experiments were performed to explore the role of waveguiding in gain narrowing experiments with conjugated polymers. A BuEH-PPV/glass sample which was too thin (43 nm) to show line narrowing as an asymmetric waveguide in air was immersed in a solvent that did not dissolve the polymer and which was approximately index matched to the glass substrate (cyclohexanone, $n = 1.49$). This produced a configuration with a symmetric waveguide structure (glass/polymer/solvent), where no minimum film thickness for waveguiding is expected.[22] Once in the solvent, the film showed dramatic line narrowing. This process is reversible: removing the film from the index matching solvent and drying caused the laser-like behavior to disappear. This observation eliminates other possible explanations for the thickness dependence of the gain narrowing, such as loss of optical density as the film thickness decreases. This result also proves that the thin film waveguide structure is critical to the production of gain narrowing in these films: even with the presence of stimulated emission and a sufficient density of chromophores, the optical path of the emitted light does not exceed the gain length at low pump energies without waveguiding. Finally, this observation also eliminates the possibility of superradiant emission as the mechanism of gain narrowing[17] since there is no simple way the coupling between the emissive dipoles in the polymer film could be altered by merely changing the index of refraction of the external medium.

With waveguiding in the polymer film, it seems surprising, at first, that there is little angular dependence to the gain narrowing. Since the guided light is nominally confined to the plane of the sample, one might expect to observe gain narrowing only in the plane of the sample. The glass substrates used, however, are not optically flat, and even on optically flat sapphire substrates, the thickness of the spin-cast polymer film typically varies by ~10%. Moreover, since the films were not spin-cast in a clean room environment, dust particles are almost certainly present. These irregularities in the films and their surfaces lead to imperfections in the waveguide which allow the light to escape. Thus, although the waveguide extends the path length in the gain medium, the guided light scatters out of the film and can be detected even along the sample normal. This picture provides a rationalization for the observation of the essentially isotropic nature of the gain narrowed spectrum in the thin film polymer samples.

III. Comparison of Gain Narrowing in Waveguides and Microcavities

A detailed comparison of the emission from conjugated polymer lasers constructed from microcavities (thin film polymer layer between a highly reflective distributed Bragg reflector, DBR, and a silver mirror) to the gain-narrowed PL produced in planar waveguides (thin polymer film spin-cast onto glass) was recently completed, and the use of hole-transporting cladding layers to achieve gain narrowing in the presence of ITO on the substrate was explored.[24] Although ITO suppresses the waveguiding, insertion of a layer of poly(*N*-vinylcarbazole) (PVK) between the PL polymer and the ITO restores the waveguiding and the gain narrowing. The quality of the microcavity polymer laser is strongly dependent on matching the microcavity mode to the gain maximum of the PL polymer, but is insensitive to whether the PL polymer or PVK is in contact with the silver layer. Because the threshold for gain-narrowed emission is the same in waveguides and microcavities, there are advantages for each approach.

We focus on BuEH-PPV,[25] a soluble alkyl-substituted PPV with a high PL efficiency (η_{PL}) of 62% in neat films and bright yellow/green EL in polymer light emitting diodes (LEDs), $\eta_{EL} \approx 2\%$ ph/el, and light emitting electrochemical cells (LECs), $\eta_{EL} \approx 3\%$ ph/el.[12] BuEH-PPV is a particularly promising laser material, with a relatively long SE decay time (≈ 60 ps),[26,27] and gain narrowing thresholds below 10 μJ/cm^2 in planar waveguides.[11,12] The DBR mirrors have nominally greater than 99% reflectivity at normal incidence from 488 to 694 nm. The high reflectivity over such a broad wavelength range results from the many layers with different layer thicknesses (chirped DBR) such that longer wavelengths are reflected deeper inside the stack. As a result, the microcavity supports several modes.

Waveguides and microcavities consisted of simple layered structures: glass/BuEH-PPV/air or glass/ITO/PVK/BuEH-PPV/air for the waveguides and DBR/PVK/BuEH-

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PPV/Ag or DBR/BuEH-PPV/PVK/Ag for the microcavities. The use of optical waveguides for gain narrowing and the basic experiment used to characterize the optical waveguides were described in previous sections. Results from BuEH-PPV waveguide structures, with and without ITO as well as with PVK cladding layers of two different thicknesses, are presented in Fig. 4. The PL spectrum shows gain-narrowing with a well-defined threshold; the waveguide with BuEH-PPV on glass has the lowest threshold, ≈ 0.05 μJ/pulse (10 ns pulse focused to ~1.5mm). In contrast, when ITO is in contact with the BuEH-PPV layer, the gain narrowing threshold is increased by about three orders of magnitude.. When a PVK layer is introduced between the ITO and BuEH-PPV, gain narrowing is restored; the threshold decreases from 2 μJ/pulse to < 1 μJ/pulse as the PVK layer thickness is increased from ~90 nm to ~340 nm.

The ITO electrode suppresses gain narrowing by preventing the formation of a planar waveguide.[11,12] Because of the high index of refraction of ITO ($1.8 \leq n_{ITO} \leq 2.1$),[28] a guided mode cannot be supported in a BuEH-PPV film ($n_{BuEH\text{-}PPV} = 1.69$)[12] on ITO. Waveguiding can be restored by use of a PVK cladding layer of appropriate thickness, a promising result for LEDs which often show higher EL efficiency when PVK is used as a hole transport layer. The conducting ITO also reduces η_{PL} of the polymer film;[29,30,31] However, polymers with η_{PL} substantially lower than that of BuEH-PPV, such as MEH-PPV ($\eta_{PL} \approx 15\%$),[29] exhibit gain narrowing in waveguides.[11,12] Thus, with $\eta_{PL} \approx 62\%$, PL quenching by the ITO electrode would not, by itself, eliminate gain narrowing.

Since microcavities have relatively high Q and efficiently couple emitted photons to only a few cavity modes,[32,33,34,35] the emission peaks are quite narrow (≤ 7 nm) even below threshold. Above threshold, the emission peak nearest the gain maximum (550 nm for BuEH-PPV) grows in intensity more rapidly than the other emission peaks as the pump energy increases. Thus, following Tessler *et al.*,[13] we define the mode ratio as the ratio of the integrated power of the lasing mode to that of one of the other spontaneous emission modes.

The emission modes from a BuEH-PPV microcavity (~340 nm of PVK between the BuEH-PPV and Ag mirror), with intensities scaled for clarity, are shown in Fig. 5. All pump energies were corrected for the transmission of the silver. There is a strong emission peak around 552 nm, close to the gain maximum of BuEH-PPV, and observable emission from four other microcavity modes. An abrupt increase in the mode ratio (see inset) is observed near 0.1 μJ/pulse, the lasing threshold. Note that the mode ratio approaches 100 at pump energies which are above threshold but still fairly low (~60 μJ/pulse). Thus, like the waveguides, microcavities can produce single-mode emission with a narrow peak when pumped above threshold.

Varying the thickness of PVK in microcavities allows control over the positions of the allowed modes with respect to the gain maximum of BuEH-PPV. We find that the mode ratio is sensitive to the positions of the cavity modes. If the PVK thickness is adjusted such that resonance occurs at the maximum gain wavelength of BuEH-PPV, the normalized mode ratio is greatly enhanced, leading to effectively single-mode emission above threshold (cf. Fig. 5). Single-mode operation is only realized, however, when the lasing peak is located within ~5 nm of the gain maximum. BuEH-PPV microcavities with lasing peak at wavelengths less than ~547 nm or greater than ~554 nm showed mode ratios of only about 5, even well above threshold. Hence, to obtain single-

Figure 4
Linewidth as a function of pump energy per pulse for BuEH-PPV–based waveguides: BuEH-PPV on glass (squares), BuEH-PPV on ITO (crosses), ~90 nm PVK and BuEH-PPV on ITO (circles), and ~340 nm PVK and BuEH-PPV on ITO (triangles).

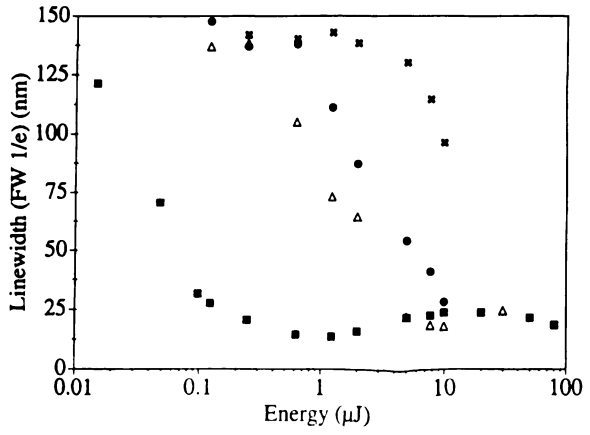
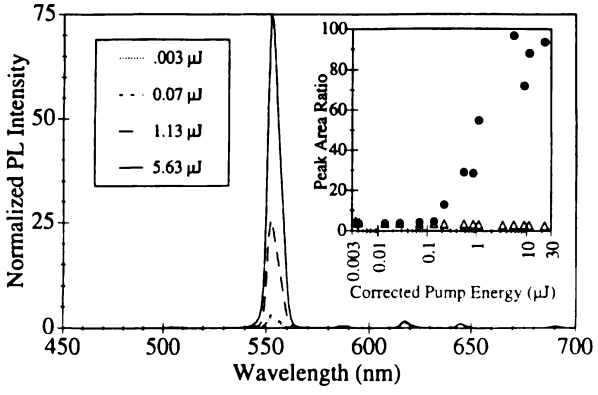


Figure 5
Emission spectra from a microcavity: DBR/BuEH-PPV/PVK/Ag at various pump energies. The PVK layer is ~340 nm thick. Inset: Ratio of integrated intensities (mode ratio) of ~552 nm peak to ~645 nm peak.



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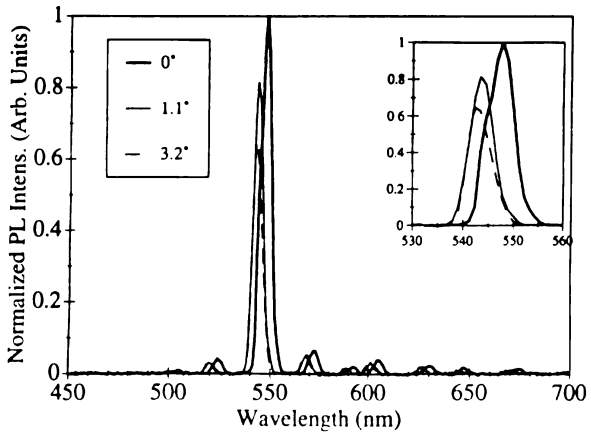
mode lasing from microcavities, the cavity design must be optimized to better than about 5 nm. This result is in contrast to the emission from planar waveguides, where single mode emission is routine.

By interchanging the order of the polymer layers, one can determine whether there is significant quenching when the active polymer is in contact with the Ag mirror. Regardless of the presence of PVK or the proximity of the BuEH-PPV to the Ag mirror, the lasing threshold was around 0.1 μJ/pulse. There was no indication that thresholds were lower for samples with a PVK buffer layer between the BuEH-PPV and Ag. Thus, although the metal electrode limits the Q of the microcavity, PL quenching by proximity to the metal is not of major importance.

The angular dependence of the emission from a microcavity with a ~900 nm PVK layer between BuEH-PPV and Ag is shown in Fig. 6. This structure showed essentially single-mode emission above threshold similar to the data in Fig. 5. To measure the angular dependence, the emitted light was collected through a 1 mm pinhole placed ~10 cm from the sample, providing angular resolution of ~0.5°. At pump energies below the lasing threshold (0.1 μJ/ pulse), the integrated emission intensity decreased by nearly an order of magnitude as the collection angle deviated from 0° to 5° from the normal, a result which indicates fairly high Q. The emission spectra shown in Fig. 6 were collected at three different angles at a pump energy (~10 μJ/pulse) well above the lasing threshold (see Fig. 6 inset). The spectra are scaled such that the intensities of the main peak at below-threshold pumping levels are normalized to the same value (the directionality that is inherent in microcavity structure has been divided out). Fig. 6 shows that above threshold, the normalized intensity of the main peak is reduced by ~35% relative to its below-threshold value as the collection angle is increased from 0 to 3.2 degrees. Thus, in addition to achieving a relatively high degree of directionality expected for microcavities, the directionality is enhanced above the lasing threshold. These observations confirm that the light emitted from optically pumped semiconducting polymer microcavities is laser light.[13]

Figure 6
External observation angle dependence of emission spectra of a microcavity DBR/BuEH-PPV/PVK/Ag. The PVK layer is ~900 nm thick. Inset: Expanded view of the lasing peak near 550 nm.



IV. Conclusions and Future Directions

In summary, conjugated polymers form a new class of solid-state laser materials with gain narrowed emissions that span the visible spectrum. Because of their strong absorption coefficients, the high density of chromophores, and the Stokes-shifted luminescence, luminescent semiconducting polymers have potential as high gain laser media with low thresholds, even in submicron thick films. The novelty of these materials was demonstrated in dilution studies, which show a highly non-linear dependence of the threshold for gain narrowing on polymer concentration. In contrast to conventional laser dyes, conjugated polymers can be useful neat and undiluted. Consequently, films of semiconducting polymers show a gainnarrowing threshold which is over 3 orders of magnitude lower than comparable solid films containing conventional laser dyes. By changing substrates and using index matched solvents, we demonstrated that the thin films constitute simple waveguide structures and that channeling of the emitted light is an important ingredient in controlling the gain narrowing of these materials.

The observation of gain narrowing in optically pumped neat thin films of a class of conjugated polymers with the aid of waveguides and microcavities offers the promise of constructing electrically pumped solid state diode lasers with a semiconducting polymer as the active gain medium. There are three major hurdles that must be overcome before this promise can be fulfilled. First, carrier concentrations sufficient to produce gain narrowing or lasing must be demonstrated by electrical pumping. Current densities of 100 A/cm^2 have been reported in electrically pulsed MEH-PPV diodes when operated in pulsed mode with low duty cycle;[36] the corresponding peak brightness was 10^6 cd/m^2.[37] In parallel experiments, current densities of 2500 A/cm^2 were reported in electrically pulsed PPV diodes when operated in pulsed mode with low duty cycle; the corresponding peak brightness was 5×10^6 cd/m^2.[38] Based on the photon densities at the optically pumped gain narrowing threshold (with ~10 ns pulses) and assuming an internal quantum efficiency for electroluminescence of a few percent, the transient current densities necessary to reach the threshold for gain narrowing are estimated to be a few thousand A/cm^2. Construction of the laser diode with a higher-Q microcavity or improved waveguiding structures should provide a further decrease in the threshold for lasing. We are presently pursuing

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several types of resonant structures, including confinement by distributed feedback,[39] with initial results that suggest that lasing thresholds can be lowered by at least another order of magnitude. Therefore, with small active areas, low duty cycles, and good thermal management, sufficiently high current densities should be accessible.

Second, the solid-state polymers that have been studied to date have short SE times which are limited by an interfering excited state absorption. While this is not a difficulty for demonstrating optically pumped polymer lasers (since gain takes place before the absorption relaxes to mask the SE), this might not be the case for injected carriers in an electrically pumped device. If such carriers have the same interchain excited state absorption as in the optically pumped samples, the induced absorption could overwhelm the SE and destroy optical gain in the device. This problem can be overcome, however, by using a material in which the excited state absorption never interferes with the SE. We are presently surveying for such suitable materials, the signature of which is an SE decay time that persists for the entire lifetime of the PL.[16]

The third challenge lies in the need to have carrier injecting electrodes, such as indium tin oxide (ITO) or metals, in direct contact with the conjugated polymer. The results summarized in Section III provide confidence that this problem can be solved.

The lasing thresholds of the microcavities (~0.1 μJ/pulse) are comparable to the gain narrowing thresholds for conjugated polymers in planar waveguides[11,12] (0.05 μJ/pulse). Thus, the optical path length within the gain medium is approximately the same in both structures. Microcavities provide the resonant feedback necessary for "true" lasing. The emitted laser light is directional and spectrally narrow. These advantages come at a significant expense, however, in device fabrication. Waveguides are easily prepared simply by spin-casting a polymer film from solution. The luminescence from the polymer is amplified when the distance traveled by the guided light exceeds the gain length. This amplified spontaneous emission is lasing in the original sense of the acronym (LASER: Light Amplification by Stimulated Emission of Radiation), but not in the more stringent sense of modern usage which requires feedback on a well-defined optical mode. Waveguides offer clear advantages for applications which require bright, isotropic, spectrally narrow emission. Microcavities work best for applications where a well-defined beam of emitted light is desired. In both structures, the excited semiconducting polymer leads to amplification with a very short gain length.

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Biographies

Professor Alan Heeger and his colleagues at the University of California, Santa Barbara, have done pioneering work in the area of semiconducting and metallic polymers. Current activities include studies of light emission from semiconducting polymers, the fundamental physics of metallic polymers, and the nonlinear optical properties of charge transfer polymers. Professor Heeger was awarded the Oliver Buckley Prize by the American Physical Society in 1983 and the Balzan Prize (Balzan Foundation) in 1995. UNIAX Corporation, founded by Professor Heeger in 1990, is focusing on bringing Plastic Electronics into commercial products.

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A High-Frequency Optical Modulator Based on Room-Temperature-Processed Nonlinear Optical Polymers

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A major step toward the goal of ambient-temperature-processed, all-polymer, high bandwidth optical modulators is reported. A Mach-Zehnder optical modulator was fabricated from a 0.8-micron thick electro-optic Langmuir-Blodgett-Kuhn (LBK) film. Polar order in the active optical waveguide was achieved using self-ordering amphiphilic polymers of the syndioregic chromophore-in-mainchain configuration (accordion polymers). This demonstration of the elimination of high temperature electric-field poling is a major milestone; however, this must now be reproduced with polymers having greater thermal stability and a greater electro-optic coefficient.

The development of economical ambient-temperature-processed all-polymer devices for information processing is an overarching goal of this project. An important military need motivating research on second-order nonlinear optical polymers (NLOPs) (1) is optical modulation at microwave frequencies for remote antenna links via fiber-optics (2). EO polymer films can be coated onto silicon, etched to form optical waveguides, patterned with electrodes to form a Mach-Zehnder modulator, and monolithically integrated with light sources (3). When the antenna signal (an electric field) is applied across the NLOP film (in the Mach-Zehnder modulator), it changes the index of refraction of the NLOP film, hence the film is also called an electro-optic (EO) polymer film. They can modulate optical signals at the highest bandwidths of any known material because of their flat dielectric response (KHz to microwave frequencies) (4).

In order to modulate the index of refraction of a polarizable film with an electric field, the film must have macroscopic polar order (5). The most common method to impart macroscopic polar order in a chromophoric polymer film is to apply a strong electric field across the film heated near its glass transition temperature (T_g), whereupon the dipole moments of the chromophores align with the electric field (6). To avoid catastrophic failure, one must be very careful to stay below the film's dielectric breakdown temperature. Polar order is locked in place by cooling the film well below the T_g before removing the field. High temperature poling can damage the film causing unacceptable optical loss. There are several types of molecular self-ordering processes being developed (7). We have focused on the room temperature Langmuir-Blodgett-Kuhn (LBK) technique (8,9).

Penner, et al, fabricated a 0.5-micron thick LBK film from side-chain second-order nonlinear optical polymers of high optical quality, and demonstrated frequency doubling

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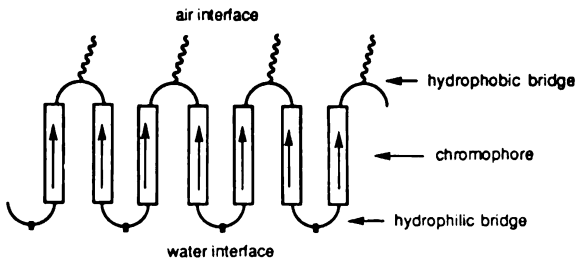
properties (10). For amplitude (or phase) modulation of the near infrared wavelengths used in fiber-optic communications, EO films of at least about one micron thick are needed. Some 600 or more LBK monolayers are required per micron of film thickness. Here we report here on room-temperature LBK fabrication of EO polymer films made from accordion polymers, and the fabrication of a Mach-Zehnder optical modulator (11) incorporating an LBK film between epoxy cladding layers as the active optical waveguide.

Accordion Polymers

Typical NLOP chromophores have a large ground-state electric dipole, and have their electronic charge-transfer axis nearly parallel with their long geometric axis. We have focused on developing mainchain NLOPs comprised of chromophores connected at both ends of their long axis and linked together by special bridging groups in head-to-head pairs along the polymer backbone (the mainchain syndioregic topology) (12). Very encouraging EO activity has been obtained using this topology in poled polymer films (13), but accordion polymers also show promise for room temperature thin film processing. The bridging groups linking the chromophores can be functionalized to add hydrophilicity, hydrophobicity, hydrogen-bonding, cross-linking, etc. By designing bridging groups for specific molecular interactions, one can create conditions favorable for the polymer chains to assume a folded polar conformation, hence the term "accordion" polymers (Fig. 1).

Designs that promote stable noncentrosymmetry are required for EO films. Y-type deposition, in which the monolayers are deposited on the up-stroke and the down-stroke, yields the most stable LBK film configuration by mating surfaces of like energy (8). We have chosen an -$(AB)_n$- bilayer structure in which the chromophore in polymer A has its electron-donating end connected to a hydrophobic bridging unit, and its electron-accepting end connected to a hydrophilic bridging unit; and the chromophore in polymer B is connected in the opposite sense.

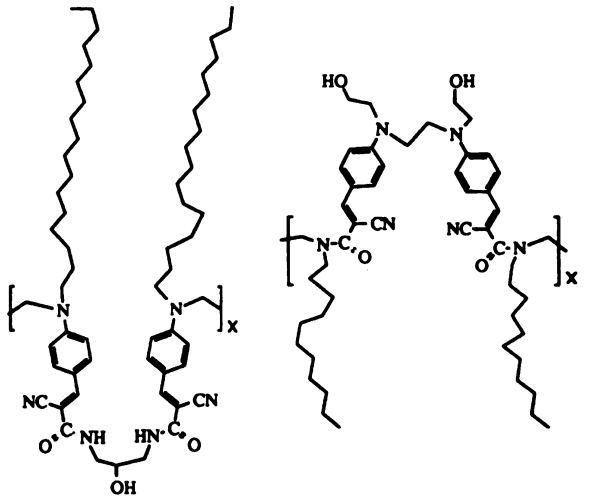
Figure 1
A floating monolayer of amphiphilic accordion polymer



The synthesis of two such amphiphilic accordion polymers, **A** (12) and **B** (14) (Fig. 2 and cover picture), was based on a Knövenagel condensation of a bis(aryl aldehyde) electron-donating monomer and a bis(activated methylene) electron-accepting monomer (15). The aliphatic chains in **A** contain 16 carbon atoms, and in **B**, 12 carbon atoms (16).

The electronic absorption maximum for thin films deposited on glass for **A** and **B** are 429 nm and 406 nm, respectively. The number average molecular weights (M_n) of these polymers were determined by aldehyde end group analyses from proton nuclear magnetic resonance (H^1 NMR) spectroscopy (17). The number-average molecular weights of **A** (sample 1500-17) and **B** (sample 1500-22) used in all of the films of this study are about 50,000 g/mol and 10,000 g/mol, respectively. Polymer **A** was purified by preparative gel permeation chromatography.

Figure 2
*Amphiphilic accordion polymers: **A** (left) and **B** (right).*



No indication of cyclic oligomers were observed by GPC. The molecular weight per repeat unit (two chromophores) is 905 g/mol for **A** and 859 g/mol, for **B**. Differential scanning calorimetry showed that **A** has two thermal transitions, a low one at 18°C and a higher T_g at about 92°C (the lower transition probably due to associations of the long aliphatic chains from the cinnamamide segments). Similarly, **B** has a transition at 18°C and a higher T_g at about 66°C (14).

Film Deposition

A two-compartment circular LB trough from NIMA (Coventry, UK) was kept in a glove box in a class 100 clean room. The glove box was purged with nitrogen gas during

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the LBK film depositions at 24 °C (18). The compressed films were aged for about 5 minutes at 20 mN/m to assure densification and to assure no leakage of polymer from the compression area (Fig. 3).

The area per chromophore (half the area per repeat unit) from the pressure-area isotherms was in good agreement with the foot print of a chromophore standing nearly normal to the water surface, and agrees with what has been observed for non-polymeric systems (19). This also precludes the possibility of multi-layering before and during deposition. Films were deposited on hydrophobic microscope slides at a rate of about 2 to 3 mm/min (**A** on the down stroke) (20).

Optical Measurements

Linear absorption and second harmonic generation (SHG) intensity were measured in transmission on a freshly prepared films of 19 and 92 bilayers in thickness (21). The increase in linear absorption and square root of SHG intensity as a function of the number of bilayers indicated that the films have a high degree of uniformity in thickness and in polar alignment (22). Complete 360° SHG scans about the azimuthal angle were recorded for 6 different polarization combinations of the incident fundamental and detected second harmonic beams. These combinations were (fundamental → second harmonic): p→p, s→p, p→s, s→s, and 45°→p, and 45°→s. The results indicated complete symmetry in the plane with point group ∞mm (22).

For the 92-bilayer film the transfer ratio for **A** was about 0.5 and for **B** was about 1.05. The second-harmonic coefficient, d_{33}, was determined by the Maker-Fringe technique (23) to be about 4 pm/V. The $\beta(0)$ of the chromophores was estimated to be about 15 x 10^{-30} esu by MOPAC® calculation (24). The thickness of the film was 2900 Å ±300 Å by profilometry (Tencor Alpha-Step). Thus, the average thickness of a monolayer is about 16 Å. We have not yet determined if the aliphatic chains between layers are interpenetrated, nor if any void volume is trapped between **B** layers due to incomplete transfer of **A**.

The Optical Modulator

A push-pull modulator (11) was fabricated to demonstrate the feasibility of using a room temperature processed film for the EO core layer (Fig. 4). For guiding 1.3 micron light in a buried waveguide Mach-Zehnder modulator (MZM), an EO film nearly one-micron thick was needed. To make the MZM, an E-beam-evaporated gold ground plane (2500Å) was deposited onto a glass substrate and then coated with a 10.3-μm layer of UV-cured optical epoxy (NOA 81 from Norland) which served as a lower cladding. The active core material was then applied to this structure to form the bottom half of the MZM. The active core material, an $(AB)_{309}$ LBK film, was deposited on the lower cladding surface (taking about two weeks) (25). Channel waveguides were formed in the core layer by the following photobleaching technique. The waveguide patterning was accomplished by a non-contact projection printing method (2). A negative image was used such that the exposed areas were outside the waveguide. Exposure of the material to light of 436 nm in wavelength caused a lowering of the refractive index to provide the op-

Figure 3
*Pressure-area isotherms at the air/water interface (one repeat unit contains two chromophores): **A** (left) was compressed at 9 cm²/min at 23°C; and **B** (right) was compressed at 10 cm²/min at 24°C.*

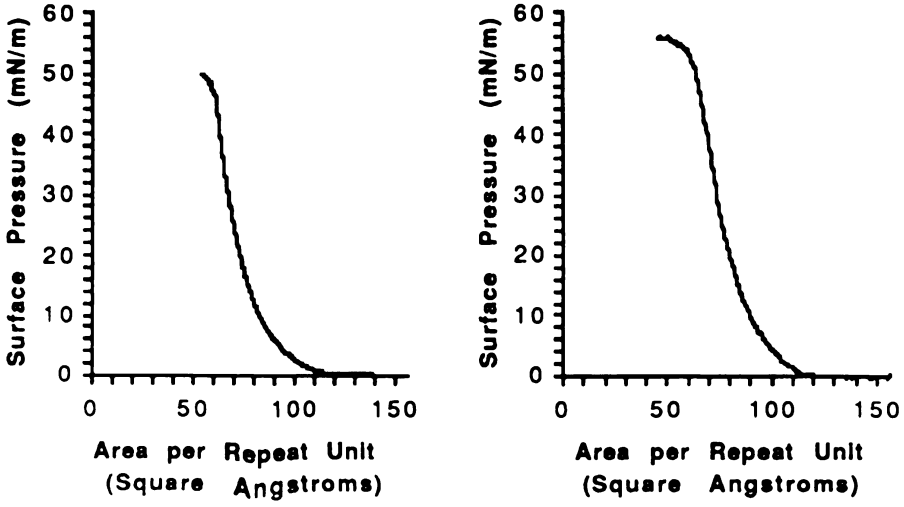

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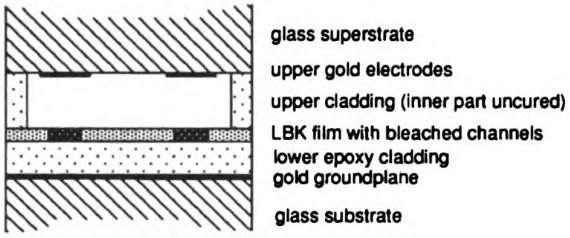
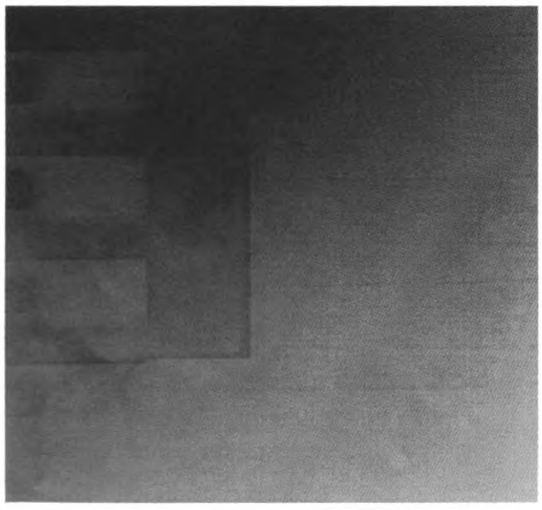
Figure 4
Schematic cross-section of buried LBK Mach-Zehnder modulator.



tical confinement in the lateral direction. Gold electrodes were patterned by chemical etching on a separate glass supporting plate. The top electrode assembly was placed on top of the lower structure separated by a 15.7-μm layer of uncured epoxy to form the upper cladding. The electrodes were micropositioned to register with the two arms of the MZM. The epoxy was then UV-cured around the periphery of the MZM taking care not to further expose the optical waveguiding regions (Fig 4). The end faces were then diced and polished near the edge of the cured upper cladding region to form the input/output surfaces for optical coupling. The thickness of the LBK film was estimated from optical microscopy of the polished end face to be about 0.8 microns. Electrical access to the electrodes was achieved by offsetting the glass plates forming the substrate and superstrate (not shown in Fig. 4).

Figure 5
Buried LBK $(\mathbf{AB})_{309}$ film in a Mach-Zehnder modulator (top-down view).



Light was coupled into the MZM by coupling a focused laser beam (890 nm wavelength) into the polished edge of the waveguide (end-fire coupling). The output imaged light was collected by an optical fiber and detected. The EO coefficient, r_{33}, was determined to be 1.1 pm/V. The faint lines of the channel waveguides in the polymer can be seen emerging from under the patterned electrodes in a photograph of the top view of a portion of the completed modulator (Fig. 5).

Aging Study

Using the LBK conditions described above (26), $(\mathbf{AB})_{10}$ and $(\mathbf{AB})_{20}$ films were prepared on glass microscope slides for a room temperature aging study (approximately 24 °C) in air and in nitrogen, respectively (Fig. 6). All films were stored in complete darkness. SHG measurements, performed as described above, were taken in the dark in air. The samples stored in nitrogen were exposed to air during SHG measurements for about 15 minutes for each data point (a total of about 2 hours over the 1440 hour duration of the aging study).

Although the films differed in thickness, qualitative conclusions can clearly be drawn from the data. The $(\mathbf{AB})_{10}$ sample, aged in air, retained only 10% of its initial SHG intensity after 2-months aging. The loss is no doubt due primarily to oxidation of the chromophore. The electronic absorption of this film is completely bleached out after exposure to air for one year. The $(\mathbf{AB})_{20}$ film, stored under nitrogen, retained 75% of its initial SHG intensity after 2-months aging with minimal exposure to light and air. Most of the loss was likely due to physical aging, because the glass transition temperature of **B** was only about 40°C above the aging temperature (whereas, at least 100°C above aging temperature is required for years of stability). Some oxidation from air contamination in this sample was also likely. The oxidation problem can be mitigated by incorporating all-aromatic amine electron donating groups in the chromophore (27). The synthesis of all-aromatic amine, self-organizing accordion polymers is in progress.

In conclusion, this is the first time that process-assisted self-organization principles have been used to produce a polymer-based buried waveguide optical modulator. The EO coefficient is modest, but these results represent a step toward the goal of economical, ambient-temperature processed, all-polymer optical devices for high band-width, ultrafast information processing. Improvements are required at almost every step of our approach to achieve practical devices. At the molecular level, chromophores must be more stable to oxidation and photochemical degradation. At the polymer chain architecture level, structures utilizing self organization principles for generating intrinsically polar films must have a higher T_g and must to lend themselves to faster processing. These and other improvements are under active development.

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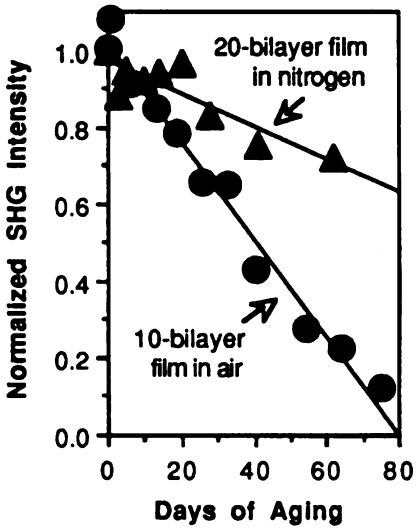
Figure 6
Room temperature aging in air and nitrogen.



Acknowledgments

The assistance of A. P. Chafin, R. A. Henry (dec.), and R. A. Hollins (synthesis), L. H. Merwin (H^1 NMR), Linda Johnson (profilometry), and of R. Y. Yee (thermal analysis) with the US Navy, Research & Technology Div., China Lake, CA is gratefully acknowledged; as is the financial support of the Office of Naval Research.

Biographies

Dr. Geoffrey Lindsay leads the group at China Lake that has been pioneering the design, synthesis, and characterization of photonic polymers for active waveguide applications since 1987. In 1995, Dr. Lindsay organized an international symposium on "Polymers for Second-Order Nonlinear Optics, " and edited a book developed from that conference with Prof. Ken Singer. Dr. Lindsay is recipient of the William B. McLean Award and the Vice Adm. Harold G. Bowen Award for inventions that contribute to the mission of the U.S. Navy.

Dr. M. Joseph Roberts, recently hired at China Lake, prepares the room temperature deposited nonlinear optical polymers (NLOP) and is an expert in Langmuir-blodgett processing.

Dr. John Stenger-Smith (batman) synthesizes the polymers and is coauthor on most of the group's NLOP publications. Dr. Stenger-Smith is also an expert on electrically conductive polymers and electrochemical switching of conductive polymers.

Warren N. Herman has been principal investigator of several research programs on optical properties of nonlinear optical polymers at NAWC. He was an adjunct faculty member of Penn State University at Great Valley, PA, where he taught graduate courses in fiber optics and advanced E&M. He previously was a staff engineer at GE Aerospace, concentrating on GaAs MMIC.

Dr. Ashley is currently the Chief of the Chemical and Material Sciences Group at the U.S. Army Missile Command (MICOM) where he has been involved in Integrated Photonics research for the past 15 years. Previously he was Director of the Electro-Optics Laboratory at Sciences Applications Incorporated. His work includes development of materials and devices in $LiNbO_3$, semiconductors, and EO polymers for military applications in sensors, signal processing, and interconnects as well as passive components including diffractive or binary optics.

Kenneth J. Wynne is Program Manager, Organic and Polymeric Materials at the Office of Naval Research. Dr. Wynne's research interests include polymer surface design and characterization, polymers with novel optical properties, electronically conducting polymers and preceramic polymers. He has published over 70 papers, has coedited three books, and has 10 patents. He was recently elected Councilor of the Polymer Division of the American Chemical Society.

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20. The glass slides (Fisher, Cat. # 12-550A) were hydrophobicized over refluxing hexamethyldisilazane (Aldrich) for about 30 minutes. Before commencing deposition, the films were compressed at a rate of about 10 cm2/min until a surface pressure of about 20 mN/m was obtained. During the deposition process, the change in surface area of each compartment was monitored and the transfer of film was made at a constant surface pressure of about 20 mN/m.
21. The linear absorption was measured normal to the films with a Cary 5E UV-VIS spectrometer. The second harmonic signal was generated from a Q-switched Nd:YAG laser (wavelength of 1.064 nm, pulse width of 10 ns, and repetition rate of 10 Hz) transmitting through the films (55° from normal incidence), and was measured with an intensified Si diode array (Tracor Northern). Each point is an average of 1500 laser pulses.
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Plastic Liquid Crystal Displays From Conducting Polymer

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Abstract

In a conventional liquid crystal display device (LCD), glass substrates coated with an indium tin oxide (ITO) layer are typically used for the application of an electric field to the liquid crystal material. For many applications, including cockpit and avionic display applications, there is a need for a LCD with plastic substrates. We have demonstrated for the first time the operation of a fully multiplexed plastic LCD (with 25,600 pixel) using conducting polymers (on plastic) as the substrates and the newly developed reflective cholesteric display technology. The resultant display has several features like light weight, low power consumption, increased ruggedness, bistability, sunlight readability and flicker-free operation. The functioning of the conducting polymer-based LCD is demonstrated and the features that make it attractive for Navy and Department of Defense (DoD) applications are discussed.

Introduction

Reflective LCD Technology

Reflective cholesteric (Ch)-LCDs are ideal for use in portable or hand-held devices to display information such as maps, text or graphics because they offer high resolution, sunlight readable images on a lightweight, low-power display. These desirable optical properties are a result of the unique features of cholesteric liquid crystals.[1-3] When cholesteric liquid crystal material is confined between two closely spaced (on the order of 5 microns) substrates, it typically assumes the planar texture. In the planar texture, the liquid crystal director (the average orientation the liquid crystal molecules point at the region in space) rotates about an axis. For the perfect planar texture, all axes are oriented perpendicular to the substrates. The twisting of the liquid crystal director about these axes creates a continuously varying, but periodic dielectric permitivity. Because of this periodicity, the material will Bragg reflect light incident on the sample when the pitch (distance over which the director rotates 360 degrees) is comparable to the wavelength of incident light. By applying an electric field to the cholesteric liquid crystal mixture, the material can be placed in the focal conic texture. In this state, the helical axes are oriented in random directions. The material ceases to reflect light and becomes transparent or weakly scattering depending on the material composition. By treating the bottom substrate with a black absorber, a pixel in the focal conic state appears black. Utilizing these developments, reflective Ch-LCDs have been made using glass substrates coated with the transparent metal ITO to apply an electric field to the material.[4-7] However for many applications, there is a need for non-breakable (rugged) and flexible displays. For these applications, the use of glass substrates is not acceptable.

An alternate approach is to use plastic substrates. But, the use of plastic substrates for liquid crystal displays has had little development. Ch-LCD technology is more forgiving in the use of plastic substrates than other LCD technolo-

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gies. Unlike TN, STN, or FLC LCD technologies, optically birefrigent plastic can be used, opening up a broad variety of plastic materials.

Conducting Polymer-Based Substrates

For any display technology regardless of the substrate, some type of electrical connection between the drive electronics and the display is required. Typically, in those efforts where plastic substrates are used, the approach is to coat ITO on the substrate rendering it electrically conducting. However, while improvements are in progress, the ITO currently coated on plastic does not adhere well, is brittle, and has a tendency to crack, particularly under constant bend conditions. Work at the Naval Research Laboratory (NRL) has led to the potential use of conducting polymers as electrodes. These conducting polymers adhere well to plastic, are not brittle, and do not break under constant bend conditions. Also, while patterning of ITO to form the multiplexed display electrodes requires complicated lithography and etching, conducting polymers have the potential for printing, thus greatly improving the manufacturability of plastic LCDs.

In this paper, we present the details of a fully multiplexed conducting polymer-based plastic, reflective LCD consisting of 25,600 pixels. The features of this plastic LCD that are relevant to cockpit applications are described.

Experiment

We have used polypyrrole films for fabricating the conducting plastic substrates. One can prepare polypyrrole films either chemically or electrochemically. While providing films with good quality, the latter technique suffers from the limitation that it requires a conductive substrate. Also, the dimension of the film grown by this technique is limited to the size of the electrode. In contrast, *in-situ* chemical solution deposition is applicable to a variety of surfaces including nonconductive ones. It is especially suitable where a substrate of large area or with various kinds of geometric shapes is required.[8] By optimizing the deposition conditions, we have been able to use the chemical solution deposition technique to prepare uniform and adhesive films on a plastic substrate. We have also been able to adapt conventional lithography techniques to pattern these films to fabricate conducting polymer electrodes.

When a solution containing an oxidizing agent like Fe(III) is mixed with a solution of pyrrole monomer, a chemical reaction occurs, forming polypyrrole. Since this product is not soluble, it precipitates from the solution as it forms. When the reaction proceeds at a controlled rate, a homogenous film can grow on a substrate that is immersed in the reaction solution. By controlling the growth time, one can prepare films of different thicknesses, and therefore, with different surface resistances and different optical transmissivities. This forms the basis for the fabrication of the two conducting polymer-based plastic substrates that are then used to fabricate the reflective cholesteric LCD.

Polypyrrole cannot be dissolved in common solvents. However, the conjugation of the polymer chain can be destroyed by strong oxidizing agents, resulting in smaller species which are soluble in common solvents. That forms the basis for patterning of a polypyrrole film by photolithography.

The polypyrrole film is first coated with a photoresist and then exposed to UV light through a photomask. After the exposure, the photoresist in the exposed area is rinsed off in a developer while the unexposed photoresist remains. Since protected by photoresist in the unexposed area, only the polypyrrole in the exposed area is etched by soaking the substrate in a bleach solution. Next the photoresist is rinsed off, and a patterned conducting polymer emerges. Finally, to prevent electrical shorting between the top and the bottom substrates of a LCD cell, an SiO_2 layer of 400 angstroms is deposited onto the patterned substrates by e-beam deposition at room temperature.

For the fabrication of reflective cholesteric LCDs, established fabrication steps used for glass substrates were transferred to processing with plastic. Modifications to processing were developed due to the unique properties of plastic such as using solvents that did not attack the plastic, using lower processing temperatures than that used for glass, developing special handling procedures due to the flexibility of plastic, and implementing techniques to remove trapped elements in the plastic substrates.

We used the vacuum fill approach to fabricate the display. In this method, a display has two substrates attached with an epoxy seal around the periphery of the display and are separated by 5 micron plastic spacers. The display is evacuated and a nematic/cholesteric liquid crystal mixture is injected in the display through a small fill opening in the seal by external atmospheric pressure.

One drive electronic approach to address a Ch-LCD is to use a sequential row address scheme, where a row is selected with a single, narrow high voltage pulse, and data placed on the column drivers. We fabricated single pixel samples to measure the electro-optic characteristics. The measurements revealed similar results as those found for devices fabricated with glass/ITO substrates ensuring the compatibility of plastic/conducting polymer devices with this drive electronics approach. To make connections between the drive electronics and the conducting polymer electrodes, we used ELFORM TAB cable. This material consists of electrically conducting lines printed to a resolution of 80 lpi on a graphite particle/polymer resin matrix deposited on a PET substrate. We developed appropriate time, temperature and pressure bonding parameters to achieve a bond with good electrical and mechanical integrity.

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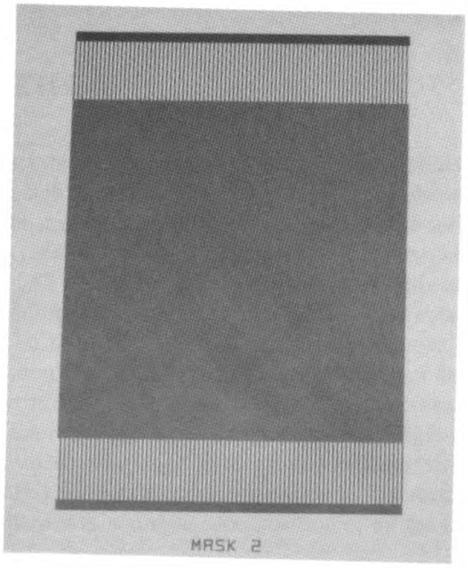
Results

Deposition of Polypyrrole Film on Plastic and Patterning

Polypyrrole cannot be dissolved or melted, so the material must be synthesized directly in the desired shape and location. For that reason, when a deposition solution is to be developed, at least two factors should be taken into consideration besides optimizing the conductivity. One is the adhesion and the other is the uniformity of the film. By optimizing the deposition solution, we have been able to prepare films with both good adhesion and homogeneity. The film can withstand the standard peeling test. SEM reveals that the film is homogenous and the typical particle size is about 100 nm. Figure 1 shows a picture of a 2 x 2" patterned substrate with a resolution of 80 line per inch prepared as described above. SEM shows that the lines and spaces are uniform and with a clean-cut edge.

In a reflective LCD device, two substrates are needed, a light or transparent one for the top and a dark or opaque one for the bottom. The typical light substrates prepared possesses a surface resistance of about 2 kohm/sq with 70-80% transmission. The dark substrate, prepared from a thicker polypyrrole film, is ideal for the bottom substrate of a reflective LCD device. It possesses a surface resistance as low as 200-400 ohm/sq with an optical transmission less than 15%. It functions as both the electrode and a black absorber which helps improve the contrast.

Figure 1
A 2" x 2" patterned substrate with resolution of 80 lpi.

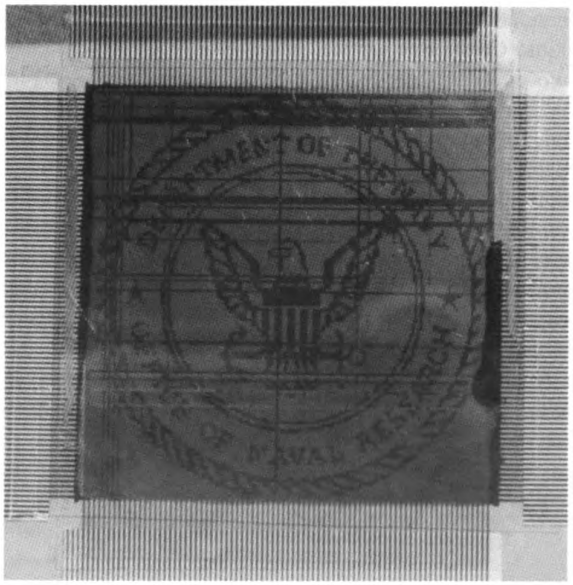


Fabrication of LCD

Figure 2 shows a picture of our first prototype display. Numerous images were addressed on the display from either the internal memory of the drive electronics or externally from a computer. The black lines on the display are either due to shorting or bad connections. This display has an active area of 2" x 2" and has 25,600 individually addressable pixels. The electrooptic characteristics of the plastic LCD have been evaluated. The response time, threshold voltage as well as the intensity contrast ratio are found to be similar to or superior to those of a reflective LCD made from glass substrates. These results will be published elsewhere.

Thus we have demonstrated for the first time the working of a fully multiplexed plastic display. This display has several unique features - it is light weight, uses less power for operation, is fully bistable and can retain an image without the need of a voltage for indefinite periods of time. Also, it does not need a back light, has a large viewing angle and is readable even in bright light. In fact, the higher the ambient light, the better the visibility. In addition, the plastic display can also be made to work in a curved configuration. All of these features make the conducting polymer-based plastic display very attractive for many Navy and DoD applications like display navigational aid, electronic manuals, hand-held and man portable displays. Efforts are in progress to increase the size as well as the resolution of the display and to shrink the driving electronics. The next generation of plastic displays with these features are expected to be demonstrated in a year.

Figure 2
A reflective Ch-LCD made from plastic substrates with polypyrrole electrodes.



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Acknowledgments

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Biographies

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Ling Huang is a contracted Research Scientist at NRL through Geo-Centers, Inc. and has a Ph.D. in Chemistry. Dr. Huang's research interests lie in surface chemistry and material science for display applications. She has specialized in organic/inorganic thin film coating and patterning as well as surface modification and the building of interface.

Catherine O'Ferrall is a contracted Scientist at NRL through Geo-Centers, Inc. and has a BS degree in Biology-Ecology, Evolutionary Biology and Behavior. Mrs. O'Ferrall is currently working on the development of patterning conducting polymer coatings on plastic substrates using photolithography techniques.

J. William Doane is Vice President for Research and Development and Chief Science Officer at Kent Displays, Inc. following his retirement from Kent State University where he was Director of the Liquid Crystal Institute. A member of the Kent State faculty since 1965 as Professor of Physics, he also served as Director of the National Science Foundation Science and Technology Center for Advanced Liquid Crystalline Optical Materials (ALCOM), a consortium of Kent, Case Western Reserve and Akron Universities. A Fellow of the American Physical Society, he has more than 200 articles and holds ten patents on liquid crystalline materials and devices.

William J. Fritz received a Ph.D. in Physics from Kent State University with emphasis on investigating the basic optical properties of the imperfect planar texture of cholesteric liquid crystals and developing approaches to improve the display properties of this material. At the Liquid Crystal Institute, Dr. Fritz is conducting research and development on various aspects of the reflective Ch-LCD technology.

Steven W. Smith received his M.S. in electrical engineering in 1996 from Case Western Reserve University (CWRU). At CWRU he worked in Microelectromechanical systems (MEMS) and micro-optical-mechanical systems (MOMS). He joined the Liquid Crystal Institute at Kent State University as a Display Engineer in 1996.

Richard Hewitt received his B.S. degree in electrical engineering at Ohio State University in 1995 and is currently employed at the Liquid Crystal Institute at Kent State University. Prior to earning his bachelors degree, Mr. Hewitt worked in Ohio as an electronics technician at Columbus Instruments for two years and was later employed by the Physiology department at OSU while completing his BSEE degree. His current work focus is the development of low cost drive circuitry for reflective Ch-LCDs.

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Novel Photoprocessing Using Photo-dynamic Azobenzene Polymers

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Abstract

Surface relief gratings were directly photofabricated in a single step on polymer films containing azobenzene groups in the side chain or in the main chain. Large surface modulation (>6000 Å) and high diffraction efficiency (>40% into each of ± 1 order) could be obtained under optimal recording conditions. Recording of the gratings was strongly dependent on the polarization of the writing beams. The localized variations of magnitude and polarization of the resultant electric field in the film are essential to the formation of the surface relief gratings. Fabrication of multiple gratings on the same spot of the polymer film was demonstrated. Fourier blazed gratings were also fabricated. The resulting surface pattern was a simple superposition of all the interfering recording waves.

Introduction

Azobenzene containing polymers are widely employed in a variety of research fields. The rigid rod-like azobenzene groups can act as a mesogenic unit and a number of liquid crystalline (LC) polymers with azobenzene groups have been reported [1]. The azobenzene chromophores have also been extensively used over the past decade in designing both third order and second order nonlinear optical (NLO) polymers [2]. Azobenzene-doped, or covalently attached polymer systems have also been studied as optical data storage medium [3]. Photo-induced orientation of azobenzene groups and photophysics associated with the trans-cis-trans isomerization has been explored in a number of other special applications.

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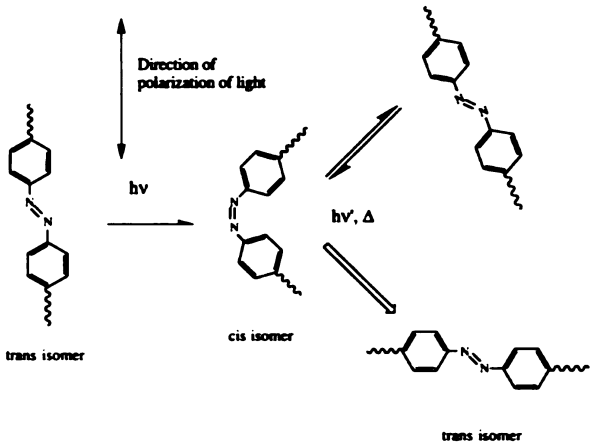
In this article we will focus on recent observation and exploration of a novel photoinduced macro scale polymer transport process observed in azo polymers. During the course of recording holograms in azobenzene-based NLO polymers, we have observed and reported photo-induced surface relief grating formation. This was observed for both films containing azobenzene groups in the side chain as well as in the main chain.

Optically induced birefringence in azo polymers

Optically induced orientation of azobenzene groups in polymer matrices was first demonstrated in 1984 by Todorov et al. [4]. They also demonstrated reversible holographic phase grating formation using this optically induced birefringence. They used azo dyes (methyl orange and methyl red) doped poly(vinyl alcohol). When the polymer system is irradiated with a linearly polarized laser beam with a wavelength of 488 nm, the optical transmission for light polarized along the polarization direction of the writing beam increased and that for light perpendicular to the direction of the writing beam decreased. Optical dichroism as well as birefringence was induced. However, long term stability was not achieved due to thermal relaxation of oriented dye molecules even when the material is stored in the dark.

The laser induced optical dichroism and birefringence was a result of induced orientation of azo dyes. The mechanism proposed for this phenomenon is related to the trans-cis-trans isomerization process of the azo groups in the polymers [4]. The azobenzenes are highly anisotropic molecules. Thus, photoexcitation of the azo group is most probable when the molecule is parallel to the polarization of the light while the azo group will be inert to photoexcitation if its orientation is perpendicular to the polarization of the light. With a polarized laser beam, the groups parallel to the polarization direction of light have the highest isomerization probability. Thermally induced cis-to-trans isomerization spontaneously follows, and the resulted trans azo groups may orient in any direction having lost their orientational memory. However, those azo groups with a component parallel to the polarization direction of the incoming light will be continuously subjected to this trans-cis-trans isomerization process while azo groups which relaxed back to a direction perpendicular to the polarization of the light will remain in this position. The final state of the material is the state with an excess of azo groups perpendicular to the direction of the light, which means a net orientation of the azo groups in the polymer matrix. The schematic explanation of the polarized light induced orientation of azobenzene groups is presented in Figure 1.

Figure 1
Schematic explanation of the polarized light induced orientation of azobenzene groups.



There has been a lot of interest in this area since Eich et al. demonstrated optically induced birefringence and reversible holographic optical storage properties on some liquid crystalline (LC) azo polymer films in 1987 [5]. The optically induced anisotropic properties of the azobenzene incorporated system have been demonstrated in a variety of matrices; LC polymers, a gelatin film, azo-dye doped polymers, Langmuir-Blodgett films and amorphous azo polymers among others [5-10]. Using this photoinduced reorientation (birefringence) process, Eich et al. demonstrated stable and erasable holographic phase grating formation in LC polymers [5,6]. They reported a maximum diffraction efficiency of 50 % in thick phase gratings and high resolving power (>3000 lines/mm). Erasability-rewritability and long-term stability for more than two years at ambient are also reported.

After the exploration of the optically induced reorientation phenomenon in azo LC polymers, amorphous azo polymers with relatively high T_gs (> 100 °C) have been synthesized and tested for optically induced orientation process [10]. High T_gs are obtained by using very short or no spacers between the main chain and the azo side groups. This results in a significant increase in the stability of the induced orientation. Natansohn et al. reported an induced birefringence of about 10^{-2}. It has thus been demonstrated that liquid crystallinity is not a necessary condition for a material to exhibit reversible and stable optically induced birefringence. The writing using polarized light with wavelength of the absorbance of the azo group can be performed at room temperature in the glassy state. The orientation can be erased by either heating the polymer above its Tg or by irradiating with circularly polarized light.

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Novel photo-induced polymer transport process

As discussed earlier, this photoinduced orientation of azobenzene groups has been studied in various polymer matrices and also employed to produce *birefringence* gratings by a number of research groups. We were surprised to observe and reported direct photo-fabrication of large amplitude (>1000 Å) holographic surface relief gratings on epoxy-based NLO polymer films containing azobenzene groups [11-14]. These surface relief gratings were produced upon exposure to an interference pattern of Ar^+ laser beams at modest intensities without any subsequent processing steps. The gratings were very stable when the polymer was kept below T_g. The gratings could be erased by heating the polymer above T_g. This *surface relief* grating formation in azo polymers has only been reported by us and independently by Natansohn and Rochon [15,16] very recently. We have clearly shown that in addition to the photoinduced orientation of azo chromophores in these polymer films there is large scale macromolecular motion leading to the formation of the relief structure.

Figure 2 shows chemical structures of the polymers on which the surface grating formation was investigated.

All the side chain polymers, PDO3, PNA, PNB, PNS, and PNI, were synthesized by reacting diglycidyl ether of bisphenol A and various chromophores [17]. The Tgs of these polymers were about 100 °C. An azo polymer CH-1A-CA was synthesized by post azo coupling reaction [18]. The Tg of the polymer was 93 °C. A main chain azo polymer PU1 was synthesized from the reaction of diaminoazobenzene and isophorone diisocyanate [19]. The Tg of the PU1 was 197 °C. All these polymers were amorphous. Good optical quality polymer films were prepared by spin-casting on glass slides. The films were dried at 70 °C under vacuum for 12 hours. The typical sample thickness of the films was ranging from 0.4 to 0.8 μm.

The experimental setup for the grating fabrication is shown in Figure 3. A linearly polarized laser beam at 488 nm from an Ar^+ laser was used. The polarized laser beam passed through a halfwave plate, and then was expanded and collimated. Half of the collimated beam passes through another halfwave plate and is incident on the sample directly. The other portion of the beam is reflected onto the sample from a mirror. Laser beams with various polarizations (defined by an angle α, which is half of the angle between two polarization respect to s-polarization) were achieved by rotating the first halfwave plate. By replacing the halfwave plate with a quarter wave plate, a circularly polarized beam could be obtained. By selecting either $\alpha=0°$ or $\alpha=90°$ and positioning the second halfwave plate in one of the recording beams, two orthogonally polarized recording beams could be obtained. This recording condition is called polarization recording in this paper. The intensity of the recording beam employed ranged from 3 to 110 mW/cm². In most cases, the

Figure 2
The chemical structures of the polymers on which the surface grating formation was investigated.

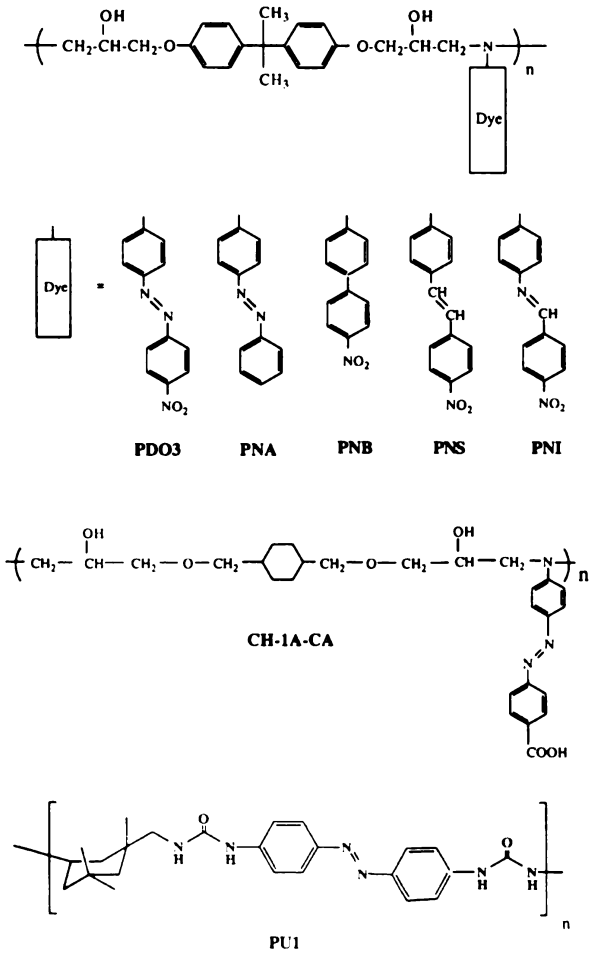
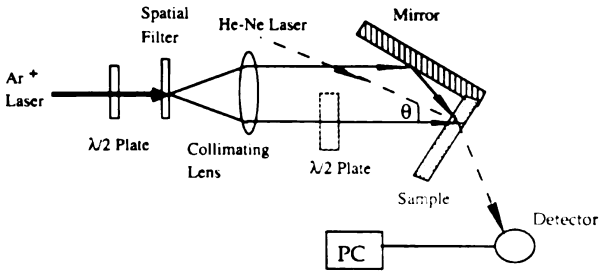


Figure 3
Experimental setup for the grating recording.



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incident angle θ of the recording beams was selected to be 14°, resulting in grating spacing of about 1 μm unless otherwise mentioned. The diffraction efficiency of the first order diffracted beam from the gratings in transmission mode was probed with an unpolarized low power He-Ne laser beam at 633 nm.

What chemical structure is required?

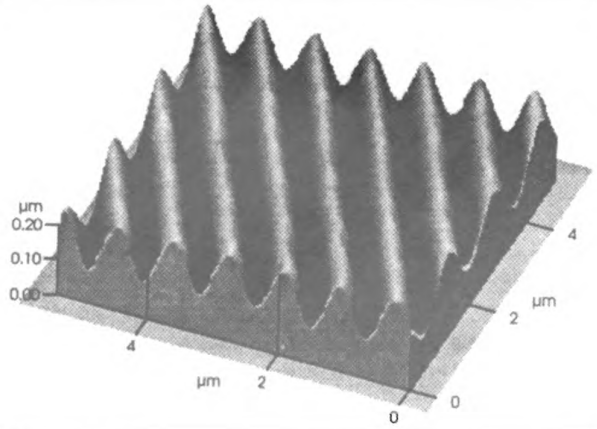
Surface relief gratings with large surface modulations could be formed on the polymers with azobenzene side groups, such as PDO3, PNA and CH-1A-CA. Surface relief gratings on polymer films were investigated by atomic force microscopy (AFM). A typical three-dimensional view of the surface gratings on the polymer, PDO3, is shown in Figure 4. As shown in Figure 4, the surface gratings showed very regularly spaced sinusoidal surface relief structures with a depth modulation of over 1000 Å. The original film surfaces before exposure to the writing beams were planar with just tens of angstroms fluctuations in the depth without any regular periodicity. The grating spacing could be controlled by changing the angle (2θ) between the two writing beams and was consistent with the theoretically calculated spacing for the interference pattern. It is clear that the surface relief patterns were produced by the interfering laser beams. Under the optimum condition, surface modulation depth greater than 6000 Å could be produced.

Among the side chain azo polymers, PDO3, PNA, and CH-1A-CA showed the formation of large surface relief gratings. In case of the biphenyl side chain polymer, PNB, surface grating was barely observed under the same exposure level. When it is considered that the polymer PNB has the same backbone structure as PDO3 and PNA, we can infer that the presence of azobenzene side groups which can undergo *trans-cis* photoisomerization is a critical structural requirement for the surface deformation process. PNA was less efficient for surface grating formation than PDO3. It may be attributed to lower optical density of PNA at the writing wavelength. Furthermore the acceptor substituted azo chromophore is expected to have a shorter excited state lifetime and hence cycle more often in the same time frame. It appears that strong electron donor-acceptor structure of the chromophore is helpful but is not a critical factor for the surface grating formation. The polymer CH-1A-CA, which is a water-soluble (alkaline pH) polymer, also showed as efficient surface grating formation as PDO3.

We also investigated the polymers with stilbene (PNS) and imine chromophores (PNI). These chromophores are known to be able to undergo trans-cis photoisomerization process as well. However, the amplitude of surface grating produced was not appreciable in these polymer films. In addition, photo-induced orientation process of chromophores was not observed with these polymer films either. It is probably because both stilbene and imine groups require larger free volume (about 224 $Å^3$) for the photoisomerization compared to the azobenzene groups (127 $Å^3$) [20]. In these type of moderately high Tg polymer matrix, there may not be enough free volume for the photoisomerization of the stilbene and imine chromophores. Natansohn et al reported very similar results from acrylate-based polymers (Tgs at around 100°C) with DR1 type azo-dyes in the side chain. They also concluded that azobenzene groups are necessary elements to observe this process.

Surface relief gratings could be fabricated on the film of the main chain azo polyurea, PU1. As expected, the formation of the surface grating was much slower than the side chain polymers as the polymer has a rigid backbone and the azobenzene groups are bound to the backbone at both ends which restrict the mobility of the chromophores. However, when it is considered that this main chain polymer has very high Tg, and relatively low absorption at the writing wavelength compared to the side chain polymers, the observation of the surface modulation is quite remarkable. We are currently investigating other series of azo polymers to further explore the effects of the structures on the surface grating formation.

Figure 4
A Typical AFM 3-D view of the surface relief grating on the PDO3 film.



How efficient are these gratings?

A typical diffraction efficiency curve of the grating on the PDO3 film monitored at 633 nm during the writing process is shown in Figure 5. The photoinduced orientation effects leading to refractive index and orientation gratings contributed to the initial increase of the diffraction efficiency. The following stage might involve the saturation of orientation grating and partial cancellation of the refractive index

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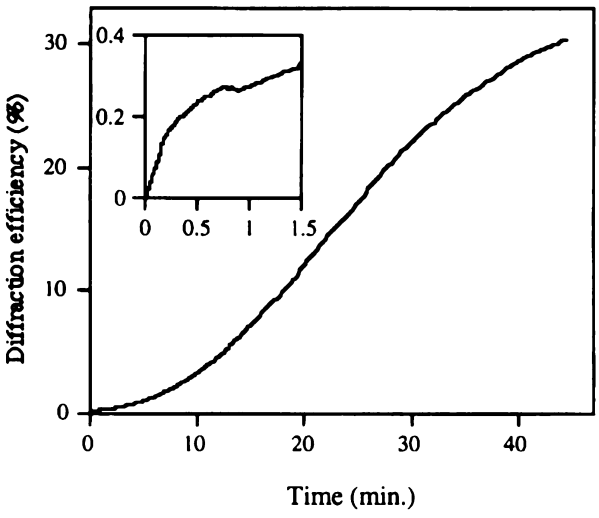
Figure 5
A typical diffraction efficiency of the grating on PDO3 film as a function of time under recording condition, α=45°. The inset shows the initial stages of the grating formation.



grating by the surface modulation [12]. In the later stage, the diffraction efficiency increased almost linearly until saturation. The increase of diffraction efficiency after the first minute or so of recording indicates the formation process of the surface relief grating. Under optimal conditions, diffraction efficiency higher than 40 % into each ± 1 order could be achieved.

Polarization states of the writing beams significantly influenced the diffraction efficiency and grating formation [12-14]. The diffraction efficiencies and surface modulations of the surface relief gratings recorded on the PDO3 film under different polarization of recording beam are summarized in Table I. All diffraction efficiency values in the table were measured at least one day after the gratings were recorded to ensure that there are no transient effects involved.

Under the condition for intensity recording (α=0°, two s-polarization), interference of the two recording beams with parallel polarization gives rise to the largest light intensity variation. However, the resultant electric field is always linearly polarized and in the direction parallel to the grating grooves over the entire irradiated area (i.e., there is no spatial alternation of direction of the resultant electric field and no component of resultant electric field along the intensity gradient). Very low diffraction efficiency and small surface modulation (<100 Å) were obtained from the grating recorded.

Under the polarization recording condition, resulting from the superposition of the two recording beams with orthogonal polarization, the greatest alternation of the resultant electric field polarization occurs on the film surface. However, the light intensity on the film is uniform over the entire irradiated area. Very small surface modulation and diffraction efficiency were also obtained under this recording condition. As the orientation grating formed, the diffraction efficiency increased, saturated and remained at a constant value throughout the rest of the recording process. After the laser beams were switched off, the diffraction efficiency decayed nearly to zero, indicating that most of the orientation grating had disappeared.

Under other recording conditions, variations of both light intensity and the resultant electric field polarization on the film exist simultaneously. Surface relief gratings could be formed, leading to much greater values of surface modulation and diffraction efficiency than those from intensity recording and from polarization recording alone. This seems to indicate that the existence of both light intensity and resultant electric field polarization variations is essential to the formation of surface relief gratings. Under the recording condition of α=45°, a diffraction efficiency higher than 40 % and a maximum surface modulation greater than 6000 Å were obtained. The gratings recorded with circularly polarized laser beams also revealed large surface modulations with high diffraction efficiencies.

Table I
The diffraction efficiency and surface modulation under different recording conditions.

Recording conditions	Diffraction efficiency (%)	Surface modulation (Å)
$\alpha = 0^{o}$	< 0.01	< 100
$\alpha = 45^{o}$	27	3600
$\alpha = 90^{o}$	15	2540
Circularly polarized	30	3500
Polarization recording	< 0.05	< 100

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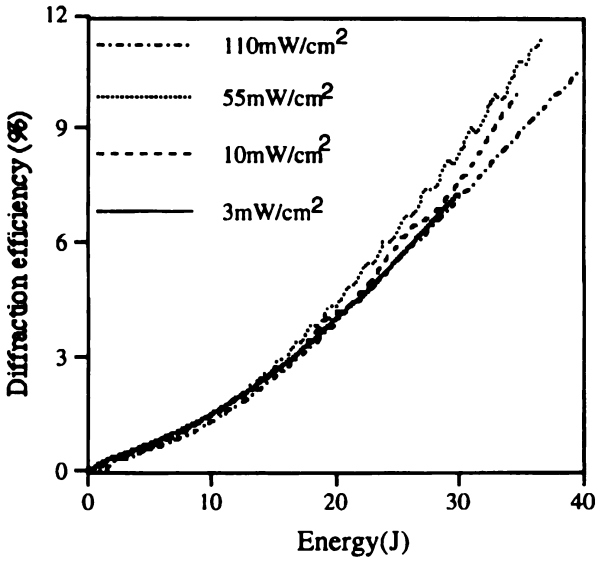
Is this process thermal or optical?

To study the dependence of the formation of surface relief gratings on the recording intensity and energy, the gratings were recorded at four different intensities viz., 110, 55, 10, and 3 mW/cm^2 respectively. Figure 6 displays the diffraction efficiencies as function of energy with different intensities of the recording beam under the writing condition of α=45°. Within the intensity range, the diffraction efficiency of the gratings is dependent only on the energy. It clearly shows that the surface grating formation process is not a thermal effect. This also suggest that the recording rate of the grating is proportional to the intensity and thus, to the rate of photoisomerization.

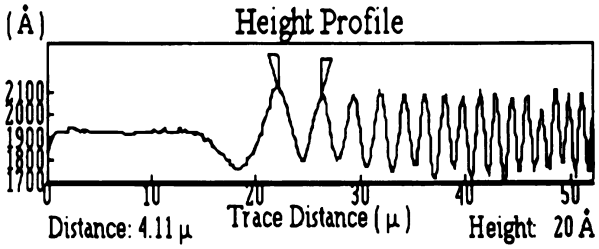
Figure 6
Diffraction efficiency of the surface grating as functions of recording power and energy.



What is the relationship between light intensity and surface deformation patterns?

To investigate the phase relationship between the diffraction pattern of the writing beams and the surface deformation patterns, a straight edge diffraction experiment was performed. The space between the edge and the film is about 100 μm. The film was irradiated by the laser beam with two different polarization, parallel and perpendicular to the edge.

Figure 7
AFM surface profile of the pattern on a PDO3 film produced by edge diffraction.

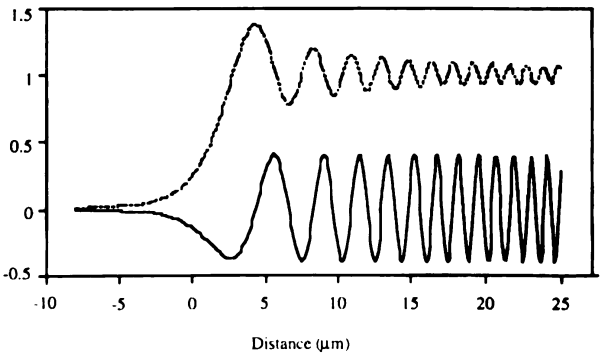


The intensity of laser beam was about 110 mW/cm^2. Similar to the result of the grating recording with s-polarized beam, when the polarization of the irradiation beam is parallel to the edge, no regular pattern of surface deformation was generated on the film. When the polarization of the laser beam is perpendicular to the edge, a regular surface relief pattern was recorded as shown in Figure 7.

The intensity distribution on the surface of the film produced by the edge diffraction can be given by the near field diffraction theory. Figure 8 displays the light intensity distribution and the negative of the first derivative of the light intensity. Comparing the modulation profile in Figure 7 and negative of the first derivative of the light intensity in Figure 8, one can clearly see that the surface profile maps the negative of the derivative of the light intensity. This can be expressed as:

$$S(x) = -\gamma \frac{dI(x)}{dx} \qquad (1)$$

Figure 8
Intensity distribution produced by the edge diffraction (dotted line) and the negative of the first order derivative of the intensity distribution (solid line).



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here S(x) is the surface profile, I(x) is the light intensity and γ is a constant.

By analyzing the results of recording of surface relief grating and edge diffraction pattern, we have found that there must exist light intensity variation in order to produce surface modulation. The grating grooves should be perpendicular to the light intensity gradient on the surface. Only when there is an intensity gradient in some direction with a non-zero component of the resultant electric field, the surface modulation pattern could be formed in this direction.

Can the gratings be superimposed? Multiple gratings.

We have also fabricated various multiple gratings at the same spot on the film. Figure 9 shows a typical AFM view of a grating with a well defined beat structure. This grating was recorded sequentially with two wavelengths at 488 and 514 nm at a fixed writing angle. In this case the period of the beat was about 19 μm. It is clear that the resulting surface pattern was very close to the simple superposition of the two recording waves. Similar gratings with the beat structure can also be written at two different writing angles at the same wavelength.

Figure 10 shows two sets of gratings recorded orthogonally to each other on the same spot on the PDO3 film. The gratings were highly symmetric and identical; the sequence of the writing was thus not distinguishable. It is evident that the formation of the first grating did not affect the formation of the next grating.

We also fabricated a Fourier synthesized blazed grating on the polymer film by superimposing two gratings with two different spacing (Λg and 2Λg). Figure 11 shows a typical three dimensional AFM view of a Fourier blazed grating fabricated on the PDO3 film.. The blazed structure is clearly seen. Two spatial frequency components, one at 1/Λg and the other one at 2/Λg, were observed as expected.

Can the gratings be made on flexible substrates?

Polymer films can also be easily coated on flexible substrates such as paper and other polymer films. Suitable organic polymers coated on paper may have potential applications in optical data storage and printing technologies in a new format.

We have coated the polymer film, PDO3, on a paper substrate and investigated the surface grating formation of that film. Waxed papers for weighing were used as substrates which were dipped into the polymer solution to coat the polymer film. Strong diffraction of ambient light from

Figure 9
AFM 3-D view of the dual gratings sequentially written with the p-polarized beams at 488 and 514 nm.

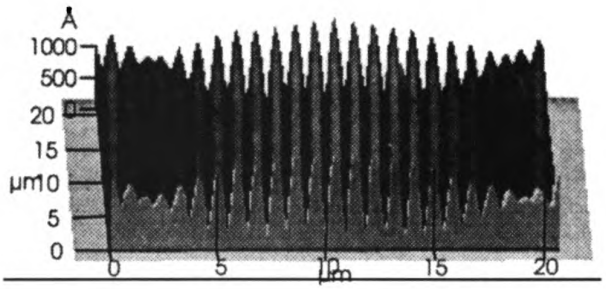


Figure 10
AFM 3-D view of dual gratings on PDO3 film recorded orthogonally to each other.

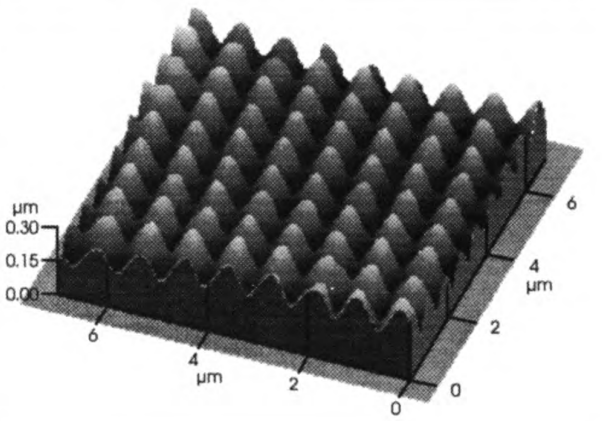
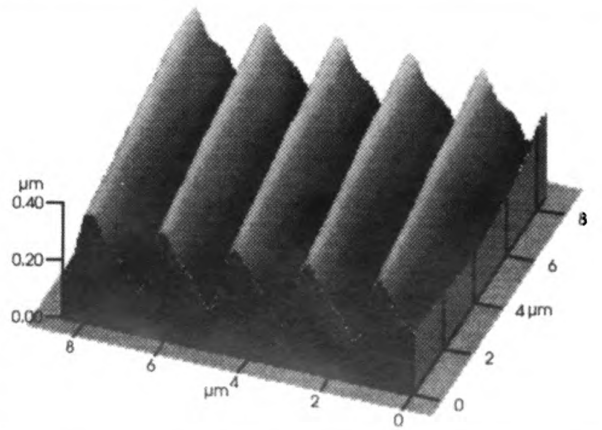


Figure 11
A typical AFM 3-D view of a Fourier blazed grating on the PDO3 film.



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the recorded film showed that large surface modulation occurred on the film. The surface of the recorded film was examined with optical microscopy. Surface relief structure on the surface was clearly seen. Diffraction efficiency in the reflection mode was measured at 633 nm. Due to the relatively nonuniform coating which is attributed to the surface morphology of paper, the diffracted beam was divergent and blurred, however, total intensity of several % in the first order diffraction could be easily measured.

Summary

Novel photo-fabrication of surface relief gratings on polymer films has been demonstrated. Large amplitude surface relief patterns could be obtained on various polymer films containing azobenzene groups in the side chain or in the main chain. High Tg main chain azo polymer also showed formation of the surface grating but the writing process was less efficient. The rate of the grating formation depends on the Tg and optical absorption of the polymers. The recording of the gratings strongly depends on the polarization of the recording beams. Under the optimal recording conditions, surface modulation larger than 6000 Å and diffraction efficiency greater than 40 % could be achieved into each of the first order Bragg mode. The diffraction efficiency of the surface gratings was dependent only on the total light energy incident on the film. From the straight edge diffraction experiment, we have found that the surface pattern mapped the negative first derivative of the beam intensity distribution. After analyzing the resultant electric field vector distribution produced by edge diffraction and by the interference of two recording beams, we believe that the existence of spatial variations of both magnitude and direction of the resultant electric field vector and nonzero component of resultant electric field along the gradient of light intensity in the films are essential conditions to induce surface modulations. We have demonstrated the formation of various multiple gratings on the same spot by simply controlling the writing wavelength and the writing angle. The resulting surface pattern was a simple superposition of all the interference recording beams regardless of the sequence of the recording. This one step surface grating fabrication process opens up new possibilities of fabrication of complex surface optical elements and devices.

Acknowledgment

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Biographies

Dr. Sukant Tripathy is Professor of Chemistry and Director of the Center for Advanced Materials at the University of Massachusetts Lowell. His research interests broadly span molecular organization and supramolecular assemblies of macromolecules, including natural substances, their electronic and optical property aspects, structural modelling, and design and development to obtain unique properties, demonstrate novel phenomenon and create new applications. He has published over 250 refereed journal articles and has over 20 U. S. patents. He was most recently the recipient of Carl S. Marvel Creative Polymer Chemistry Award by the American Chemical Society. He is Principal Investigator on a ONR sponsored MURI project.

Dr. Jayant Kumar is Professor of Physics at the University of Massachusetts Lowell. He has been Director of the Laboratory for Electronic and Photonic Materials since 1990. His research interests are nonlinear optics, laser assisted materials processing involving deposition of thin films of high T_c superconductors and other materials, magneto-optics (in particular Faraday rotation) in inorganic and organic materials, photorefractive properties of semiconductors, photorefraction in organics, dielectric behavior of conducting polymers, and optical and electronic properties of biomolecular systems. He has published over 150 research papers and holds 6 patents. He is a coPI on the ONR funded MURI.

Dr. Dong-Yu Kim obtained his Ph.D. from the Chemistry Department at UMass Lowell. His thesis research is based on novel fabrication and characterization of surface relief gratings using azobenzene polymers described in this review. He is the most recent recipient of the Unilever award sponsored by the Unilever company and ACS polymer division for outstanding Ph.D. thesis in polymer research. He is currently expanding on further application of this novel process as a research associate with Prof. Tripathy.

Dr. Lian Li is a senior scientist at Molecular Technologies Inc. He received his Ph. D. in physics from the University of Massachusetts Lowell in 1993. Over the past seven years, he has carried out research on the second order nonlinear optical, photorefractive and reversible optical storage properties of novel polymeric materials.

Dr. Xin Li Jiang received his Ph.D. in the Department of Physics at UMass Lowell under the supervision of Professor J. Kumar. His research focus is characterization of optical and electrooptic properties of polymers and fabrication of optical devices based on NLO polymers.

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Photorefractive Polymers: New Materials for the Information Age

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Abstract

In recent years photorefractive polymers have emerged as promising multifunctional organic materials for photonic technologies. The structural flexibility, ease of processing, high performance, and low cost of polymers give them a strong technological potential. Current photorefractive polymers outperform inorganic crystals such as $LiNbO_3$ and real-time holographic recording with restitution efficiencies close to unity in 100-μm-thick samples can be achieved with low power semiconductor laser diodes. That high level of performance makes them suitable for immediate applications in areas such as dynamic holographic testing and optical information processing. Here, we demonstrate one such application: an all-optical, all-polymeric optical pattern recognition system for security verification.

Introduction

As current communication systems are becoming more powerful and complex, optical technology is expected to contribute significantly to the future electronic information processing networks. The free-space nature of optics allowing highly parallel interconnects, the immunity to electromagnetic interference together with the possibility to develop high-bandwidth optical modulators and switching elements, make this new technology very attractive for the transport, the processing and the storage of large amounts of information. To make this emerging optical technology viable by the simultaneous development of enabling technologies (spatial light modulators, laser sources arrays) and new architectures, the search for novel optical materials is of crucial importance. Advances in materials are focusing on the devel-

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opment of optical materials with high optical quality, high efficiency, high sensitivity, long lifetime, low cost, and good processing capabilities. With such requirements, it is challenging to meet all these constraints simultaneously in a single material.

Among the most sensitive materials for nonlinear optical applications, photorefractive (PR) materials have been the subject of active research during the last 30 years. Discovered in $LiNbO_3$ as an undesirable optical damage,[1] the photorefractive effect has been identified[2-4] and studied mainly in inorganic crystalline materials[5] such as ferroelectrics, sillenites, and semiconductors. The photorefractive effect is based on a combination of photoconducting and electro-optic properties and can lead to high refractive index variations under the illumination of a low-power laser source. In contrast to many grating formation mechanisms with thermal, electronic or chemical origins, for instance, the photorefractive effect has a unique feature related to the transport of carriers during PR grating formation which leads to a dephasing between the light distribution that induces the grating and the resulting refractive index modulation. This nonlocal response is a fingerprint of the photorefractive effect and enables energy transfer between two coherent laser beams.[6] Many applications such as optical correlation, real-time holography, optical memories and reconfigurable interconnects have been demonstrated with photorefractive materials.[7]

More recently, the progress achieved in the field of molecular engineering, has led to the development of a new generation of photorefractive materials that are organic.[8] The field of organic photorefractive materials has been initiated in 1990 with the first evidence of the photorefractive effect in an organic crystal[9] and has grown rapidly after the demonstration of photorefractivity in a polymeric system.[10] Since the first proof of principle of photorefractivity in a polymer, the progress achieved in this new class of materials has been tremendous. Numerous PR polymer composites have been synthesized by using different synthetic approaches,[11-14] guest matrices,[15] sensitizers,[16-17] transport agents,[18] and electro-optic chromophores. However, for a long time, the index modulations generated in these materials remained too small to enable large diffraction efficiencies or to observe net gain in two-beam coupling experiments. Significant improvement in the performance of PR polymers was obtained by using the photoconductive polymer PVK as the composite host and by doping with nonlinear molecules. Such materials doped with the nonlinear optical molecule F-DEANST showed diffraction efficiencies up to 1% in 125 μm thin films.[19] The photorefractive origin of these efficient gratings was confirmed by asymmetric two-beam coupling experiments and for the first time, PR gain exceeding the absorption of the sample could be observed in a polymer. In PVK-based polymers doped with the chromophore DMNPAA and an additional plasticizer, significantly higher efficiencies (6%) could be measured in 105 μm thin samples.[20] Further improvement of this enabled the demonstration of diffraction efficiencies close to 100% and net gain coefficients exceeding 200 cm^{-1}.[21] Within the past six years, photorefractive polymers have reached performance levels comparable or, in some respect, even superior to the best known inorganic crystals.

The significance of the development of such polymers with extremely high photorefractive efficiencies can be illustrated by considering the promising properties of polymers for photonic applications in general. For a long time, organic materials have been regarded as inefficient, impure, and unstable materials for photonic applications and most of the attention was paid to inorganic materials. In the early developments of photoconductive materials for instance, most of the research effort was focused on crystalline and amorphous semiconductors such as silicon. However, within the past 25 years an intensive effort in the search of new organic photoconductors has led successfully to many industrial applications in the copier area and at present, nearly 90% of the photoreceptors are made of organic materials.[22] Organic photoreceptors for xerography has become a $5 billion industry. Likewise, organic materials are increasingly being recognized as high-performing materials for a variety of applications[23] and the misconception about the fragility of organic materials is gradually being erased by the synthesis of new materials with better environmental and thermal stability. The processability and structural flexibility of polymers give them an important technological potential and have driven intensive research efforts in the development of multifunctional polymers and molecular assemblies. Electro-optic poled polymers for instance have matured in the last few years and exhibit electro-optic coefficients[24-25] that exceed those of $LiNbO_3$ which is often considered as a standard in the electro-optic industry. In contrast to organic photoconductors, nonlinear optical molecules and polymers have not found major technological applications but the worldwide research effort under progress should ensure a gradual evolution from purely electronic devices to opto-electronic devices based on semiconductors and polymers.

In addition to the capacity to form large area films, polymers have physical properties which are favorable for the photorefractive effect. These features, including a low dielectric constant and a high electro-optic coefficient, are common to organic materials and lead to a high figure of merit for the photorefractive effect. With the tremendous progress achieved recently in this new class of materials, photorefractive polymers look attractive for photonic devices and can become an alternative to existing inorganic PR materials, especially when processing and low cost are of primary importance. Further development is expected owing to the important progress that is achieved simultaneously in the fields of molecular nonlinear optical materials and organic photoconductive materials.

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The photorefractive effect in polymers

The basic requirements for photorefractivity are that the material should respond to light by generating electrons and holes (charges) which can then be transported and trapped within the material. That charge separation leads to an internal space-charge field. The material should also have nonlinear optical properties, so that its refractive index can be affected by an electric field. Combining these properties, it is possible to write a hologram within the material using two laser beams, one carrying the image, the other acting as a reference.

When two laser beams intersect in the material, they create an interference pattern with a strongly non-uniform distribution of light intensity (see Fig. 1). Excess charges generated through optical absorption in the high intensity regions migrate to the regions of low intensity leading to charge separation and the build-up of an internal electric field. Because the material is electro-optic, the internal electric field changes internally the refractive index of the material. As a result, the initial light distribution is optically encrypted in form of a refractive index pattern in the material. The stored information can be retrieved by diffracting a laser beam on the refractive index pattern that acts as an optical grating. The diffraction efficiency η (or the hologram reconstruction efficiency) is proportional to $(\Delta n\, d)^2$, where Δn is the refractive index modulation amplitude, and d the thickness of the medium. With inorganic photorefractive crystals, a centimeter-thick crystal is usually required to get a diffraction efficiency close to unity. In comparison, the same efficiency can be achieved with 100 μm-thick polymer samples due to the high refractive index modulation amplitude that can be achieved in these materials ($\Delta n \approx 1\%$). That high efficiency is illustrated in Fig. 2 that shows the diffraction efficiency as a function of applied field measured in a 105-μm-thick sample of DMNPAA:PVK:ECZ:TNF. Another parameter that is often used to characterize photorefractive materials, is the so-called two-beam coupling gain constant. A unique feature of the photorefractive effect is the phase shift between the refractive index pattern in the material and the light distribution that generated it. This phase shift is due to the transport of the carriers that is involved in the storage process of an hologram and leads to two-beam coupling. When two coherent laser beams intersect inside the photorefractive medium, they interact through the photorefractive grating they generate and they exchange energy. As a result, one beam is amplified at the expense of the other one. This property is very useful for image amplification applications, but more important, it is the signature of photorefractivity. The observation of two beam coupling distinguishes the photorefractive effect from a variety of other physical and chemical processes that can also lead to the recording of holograms such as photochemical degradation of the material and thermal effects which are not desired. During beam-coupling experiments, the intensity of the amplified beam grows exponentially during the propagation in the sample with an amplification factor given by the gain coefficient Γ multiplied by the thickness of the sample. In order to have real amplification of one of the beams, the gain coefficient needs to exceed the absorption coefficient of the sample. This excess is called net gain. The first net gain (7 cm^{-1}) observed in a photorefractive polymer was reported[19] in 1993. One year later, our team at the University of Arizona measured[21] a net gain coefficient in excess of 200 cm^{-1} (see inset of Fig.

Figure 1

Illustration of the photorefractive effect: The overlap of two coherent laser beams creates an optical interference pattern (a). *In the high intensity regions, charge carriers are generated* (b). *One type of carriers are transported and trapped* (c), *creating an alternating space-charge field* (d). *The space charge field induces an index grating via the electro-optic effect* (e). *The resulting index grating is phase shifted with respect to the initial light distribution.*

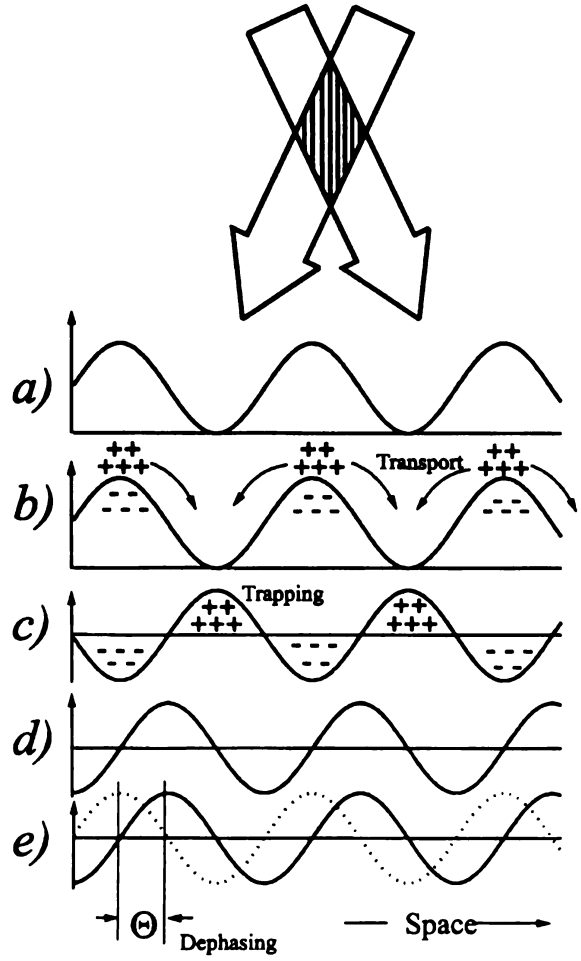

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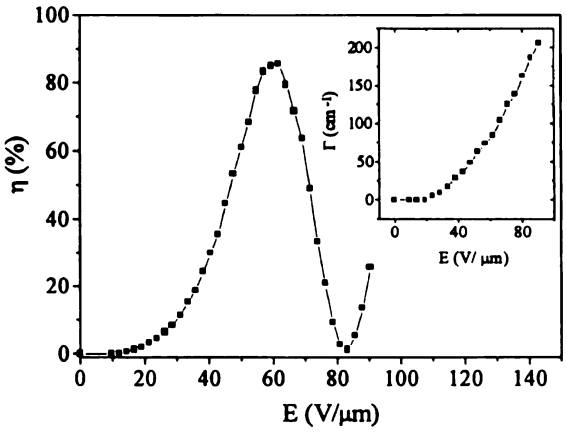
Figure 2
Diffraction efficiency as a function of applied field measured for a p-polarized reading beam at 675 nm in a 105-μm-thick photorefractive polymer (DMNPAA:PVK:ECZ:TNF; 50:33:16:1 % wt.). Inset: *Field dependence of the gain coefficient measured in two-beam coupling experiments.*



2) considerably higher than any net gain coefficient measured in inorganic crystals (30 cm^{-1} for $BaTiO_3$, one of the best crystal in that respect). This value together with the high diffraction efficiency illustrated the high efficiency of photorefractive polymers.

Initially, these high efficiencies were unexpected – calculations based on the standard models of photorefractivity had predicted efficiencies smaller than those found experimentally. New models were developed for polymers with a glass transition temperature near room temperature.[26] Effects of the reorientation of the nonlinear optical molecules in the polymer matrix by the internal space-charge field were found responsible for the high performance of these materials. This effect led to enhanced electro-optic properties and to a new contribution to the total refractive index modulation arising from the spatially periodic orientation of the rod-like molecules. Rod-like molecules have a response to the electromagnetic field of the laser light that is much stronger along their axis than in the direction perpendicular to it. This polarizability anisotropy leads to a modulated birefringence and consequently to an additional refractive index modulation. This effect tremendously improves the photorefractive efficiency and changes the figure of merit F for the dopant molecule from $F = \beta\mu/M$ for traditional purely electro-optic photorefractive polymers, to:

$$F = [A(T)\Delta\alpha\mu^2 + \beta\mu]/M \qquad (1)$$

for low glass transition photorefractive polymers. In eq. (1), β is the first hyperpolarizability, μ the dipole moment, $\Delta\alpha$ the polarizability anisotropy, M the molecular weight, $A(T) = 2/9kT$ is a scaling factor, and kT is the thermal energy. By using molecules that have a strong polarizability anisotropy such as the DMNPAA [2,5-dimethyl-4-(p-phenylazo)anisole] and by adjusting the glass transition temperature of the composite close to room temperature by adding the plasticizer ECZ [N-ethylcarbazole] to PVK:TNF-based polymers highly efficient photorefractive polymers could be developed.[21]

Due to the structural flexibility of polymers, the different functionalities required for photorefractivity including photosensitivity, photoconductivity, trapping and electro-optic activity can be combined in a polymer or composite in different ways. For example, a fully-functionalized polymer can be synthesized that contains all functional groups either in the polymer backbone or attached to it as pendent side-groups. Another possibility is to mix low-molecular-weight molecules with the desired properties into a polymer matrix. This so-called guest/host approach opens a lot of opportunities to obtain a PR polymer. The host polymer can for instance be an inert binder without any functionality, however, this choice is usually less favorable, because a major part of the material is inactive this way, diminishing the bulk photoconductivity and electro-optic properties. Therefore, in most cases the host polymer is partially functionalized. Electro-optic polymers can be mixed with a low-molecular-weight photoconductor or photoconductive polymers and with different electro-optic chromophores. Some of the components can be bifunctional and show simultaneously photoconducting and electro-optic properties as in organic photorefractive glasses developed recently.[27] Reviews of different photorefractive polymers can be found in Moerner et al.[8] and in Kippelen et al.[28]

Example of application: a polymeric optical correlator for security verification

To demonstrate the technological potential of high efficiency photorefractive polymers in device geometry, we developed an all-optical, all-polymeric pattern recognition system for security verification[29] where the photorefractive polymer was used as the real-time optical recording and processing medium. Rapid technological progress, especially in computers, CCD technology, color printers and scanners, makes forgery and counterfeit of valuable documents such as credit cards, or other important objects increasingly simple. Current techniques such as the embossed dove hologram on credit cards is no longer a reliable solution to this problem as they can be copied. Thus, there is a need for development

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of new and inexpensive optical methods for security applications[30] to better handle the counterfeiting problem. Optical security features can be inspected by either visual checking without special equipment or with the help of technical facilities for rapid screening. When such an optical system is required for security checking, low manufacturing cost is a critical issue for its technological viability.

The low cost security verification system we describe here is based on the optical encoding of documents with pseudo-randomly generated phase masks[31] and their inspection by performing all-optical spatial correlation of two phase encoded images in a photorefractive polymer in a four-wave mixing configuration. One phase image is placed on the object to be verified such as an identification or credit card. The other is made available to the security systems for comparison with the input image. The phase images may include a combination of both biometrics information for verification of the individual carrying the card as well as a secret code known to the system for authentication of the card. The practically invisible phase mask is permanently placed on the object to be verified and can be manufactured using a number of techniques such as embossing on plastic films, encoding on photopolymer, etc... With the high resolution of commercially available optical materials, the phase mask can be of the order of million pixels and the mask size will be only a few millimeter squares.

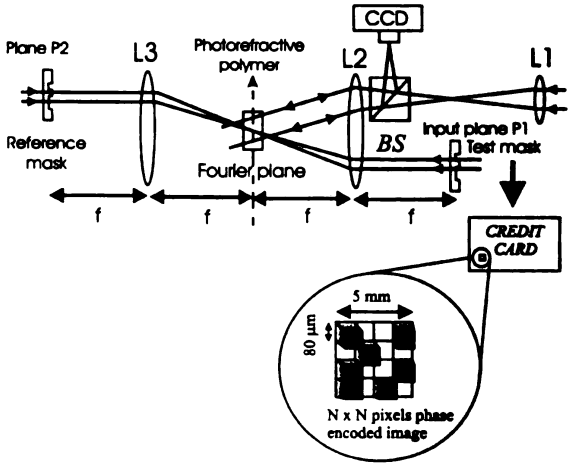
Pseudo-random codes or pseudo-noise sequences can be employed to encode the phase masks.[32] These codes have unique correlation properties: their auto-correlation is delta function like (as in the auto-correlation of white noise) with small sidelobes and with a maximum correlation value proportional to the number of the pixels in the code N. The maximum cross-correlation average between two different codes is $1/N$ times the auto-correlation peak value. Using optical materials, 2-D optical codes with large number of pixels (i.e. large N) can be employed as phase masks which results in small cross-correlation outputs for any two different codes. The auto-correlation properties of these large optical codes are used in detecting the authorized codes and the cross-correlation is used in discriminating against the unauthorized codes. Due to their correlation properties, these codes are also robust to degradation of the individual pixels. If m pixels of a code are degraded, we expect the peak to sidelobe ratio to decrease by an average of m/N compared with the original code. If $m << N$, this ratio is negligible.

The vast parallel information processing potential of optics has been the stimulus of the sustained research activity in this area. However, the limited performance and/or the high cost of existing nonlinear optical materials has severely limited the technological potential of all-optical correlators: Inorganic photorefractive crystals have been investigated[33] but their processing and high cost has limited their use in wide-spread applications. To improve processing conditions, polymers with third-order susceptibility $\chi^{(3)}$ have also been proposed in the past.[34-35] However, their low efficiency requires very high peak power laser pulses that can only be generated by sophisticated ultra-short pulse lasers sources which makes them not practical. Due to limitations of previously available optical materials, other correlator designs have been proposed over the years: nonlinear joint-transform correlators, for instance, show good performance for pattern recognition and are capable of real-time operation.[36] However, because these systems use either sophisticated liquid crystal light valves,[37] CCD detectors, and/or a computer to perform Fourier transforms, they do not meet the low cost requirement.

The proposed optical correlation system is illustrated in Fig. 3. The input card containing the phase mask is placed in the plane P1 which is to be correlated with the master phase image in the plane P2. The hologram written by the interference of the reference beam and the beam going through the test mask forms a holographic filter for the master mask. Recording of this holographic filter was performed in real time with a 633 nm HeNe laser with a total power of 1.5 mW. A separate 675 nm laser diode with < 1 mW power was used for the readout. The spatial cross-correlation func-

Figure 3

Schematic of the four-wave mixing photorefractive correlator set-up for security applications. L2 and L3 are the Fourier transform lenses (focal length 85 mm). The beams overlap in the back focal plane of the lens L2 and form an interference fringe pattern. A photorefractive polymer is positioned in the region of overlap and a phase grating is formed in it via photorefractive process duplicating the incident light intensity pattern. The signal emerges counterpropagating with the second writing beam. The diffraction occurs on the regions of the hologram where the Fourier transforms of the two masks overlap. Thus, the recorded hologram of the Fourier transformed test mask acts as a complex filter for the readout beam bearing information about the master mask. BS is a beamsplitter, CCD is a camera.



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tion of the two phase masks was formed in the plane P1. The illuminated area on the sample was about 4 mm in diameter at normal incidence. Like in regular four-wave mixing experiments, the sample was tilted at 60°. Writing beams were 's'-polarized (or perpendicular to the plane of incidence defined by the sample normal and the wavevector of the incident light, i. e., vertical in this case), and the readout beam was 'p'-polarized (horizontal). The diffracted beam was picked-up by the beamsplitter BS and was projected on a CCD camera to record the correlation. Here we used a CCD camera only to visualize the correlation peak and to compare it with the background noise. However, in practice the correlation can be verified with a regular silicon detector.

The active medium was a 105-μm-thick photorefractive polymer film sandwiched between two transparent indium-tin-oxide electrodes. For this demonstration, we used the composite DMNPAA:PVK:ECZ:TNF with the composition 50:37:12:1 % wt. The chemical structures of the components are shown in Fig. 4. A field of 50V/μm was needed during the recording of the holographic filter and the implementation of the auto-correlation. Due to its low glass transition temperature (T_g = 16 °C), this photorefractive polymer can record and retrieve optical information only when an electric field is applied. The applied field increases the photogeneration efficiency, is the drift force for the transport of the photocarriers and is responsible, together with the internal space-charge field, for the orientation of the nonlinear optical molecules. The resulting photorefractive refractive index changes through electro-optic and orientational effects are at the base of the optical recording of the holograms. The very low current (in the nanoampere range) that flows through the device, makes the power consumption negligibly small. Due to its high chromophore concentration (50% wt.), the polymer composite we used here has an average lifetime of six months at room temperature when

Figure 4
Chemical structure of the components of the photorefractive polymer use in the correlator.

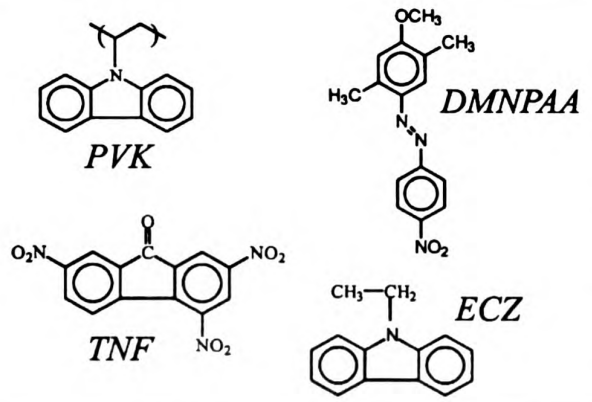

Figure 5
Amplitude version of the random binary array used to encode the document to verify.

encapsulated and protected from moisture. Chromophore crystallization and phase separation are responsible for the eventual failure of the photorefractive polymer. We have recently enhanced the lifetime of our polymers by either reducing the chromophore concentration, or by using eutectic mixes of different chromophores as we showed recently.[38] Furthermore, the stability problem can be completely solved by synthesizing low T_g side-chain functionalized photorefractive polymers. The stability of several years that can be obtained from such materials should by no means be considered as a limitation to the practical applicability of the proposed system.

For the purpose of this demonstration experiment, the phase masks were binary random patterns of 64x64 pixels, the whole array size was 5x5 mm, and was formed in a 2-μm thick photoresist layer with a refractive index of n = 1.64 deposited on a glass substrate corresponding to a phase-modulation depth of 4π. An amplitude version of the phase mask is shown in Fig. 5. In principle, larger codes and gray-level patterns can be used to improve the discriminating power. The master phase patterns can be easily composed in a phase-only spatial light modulator in real time, which allows scanning of the database of the control masks without changing them mechanically.

Figure 6 shows an example of the cross-correlation of the master phase mask with a matching phase mask. It clearly demonstrates a sharp correlation peak in the center, signifying a match. A mask different from the control image produces only the randomized background, shown around the

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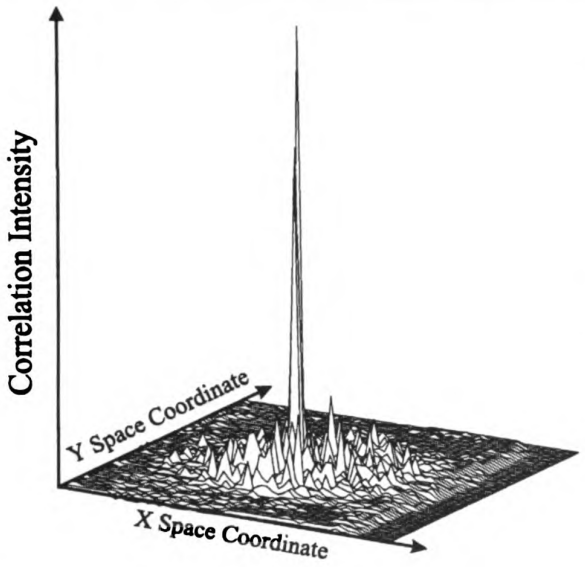
Figure 6
Spatial light intensity distribution in the correlation plane P1 with a test phase mask matching the master mask. The image in the plane P1 was captured by a CCD camera.



base of the peak in Fig. 6. Therefore, discrimination between the original and any copy is achieved by measuring the light intensity in the center of the correlation plane and comparing it with a threshold that is adjusted for a chosen security level .

The security verification system we propose has the following features that make it practical for wide-spread applications: first of all, the use of a highly efficient photorefractive polymer as active material in an all-optical correlator configuration and its compatibility with semiconductor laser diodes keep the overall manufacturing cost to levels that are significantly lower than that of any previous proposed optical correlator. The system is fast because the processing is implemented optically in parallel. Furthermore, the high resolution of the photorefractive polymers allows the use of shorter focal length lenses in the 4f correlator, thus, making its design more compact compared with one using liquid crystal light valves. In addition, all the components (including the laser source and the nonlinear material) can be manufactured in a very small size and the system can be easily further miniaturized. Finally, because the recording process is based on the photorefractive effect, the stored hologram can be erased and a new hologram can be written in real time. This reversible real-time recording and processing enables the testing of a variety of different documents encoded with different phase masks and their comparison with a corresponding master mask database. Its response time (~ 1 s) is satisfactory for the security verification tasks and does not preclude fast database searches. As explained above, use of pseudo-random codes ensures the system robustness and resistance to noise acquired during the wear.

The proposed system can be complementary to other technologies under development such as the use of biometrics for identification purposes. The phase encoding can be added to the biometric identification features such as fingerprint or picture as an additional security step. As is well established in the field of optical document security, the larger the number of available viable techniques, the better the chances of succeeding against credit card (and other value documents) fraud.

In summary, we believe that the security verification system presented in this letter possesses a number of important technical merits and advantages over previous designs that greatly increase its potential to be used in wide-spread security applications. This potential is further enhanced by the recent emergence of enabling technologies to produce very low cost precision plastic optical elements such as lenses and splitters by precision injection molding.

Conclusion and outlook

During the past six years, the progress in the field of photorefractive polymers for photonic applications has been significant. The performance of the materials could be improved by four orders of magnitude to a level where they compete or even outperform in some respect their inorganic counterparts such as $LiNbO_3$. Due to their low cost and ease of processing, these polymers can find new niche applications in optical processing technologies for civilian and military applications. Despite the high efficiencies of existing photorefractive polymers, a lot of effort is still needed to make faster materials and reduce the values of the electric field that need to be applied. In order to make the polymers suitable for holographic storage their thickness has to be increased by a factor of ten and non-destructive read-out schemes have to be developed. Owing to the progress that is accomplished in the synthesis of new molecules with better photoconducting and higher nonlinear optical properties, the future of photorefractive polymers looks quite bright at this stage. By establishing the fundamental mechanisms that govern the performance of photorefractive polymers, new materials and devices with even further improved capabilities will be fabricated. New frontiers such as self-assembly molecular approaches look particularly promising.

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necticut University for his collaboration in the correlator work, and fruitful collaboration with colleagues from the ONR funded CAMP Center.

Biographies

Nasser Peyghambarian holds the *Lasers and Photonics Chair* at the Optical Sciences Center of The University of Arizona. He is a Professor in Optical Sciences and a Professor in Materials Science & Engineering. He is currently the Director of the Center for Advanced Multifunctional Nonlinear Optical Polymers and Molecular Assemblies (CAMP) funded by ONR. His research interests include the study of nonlinear optical materials and optoelectronic devices. He is a Fellow of the Optical Society of America and the American Physical Society. He is the author of over 200 publications, one textbook, six edited research books, and several book chapters. He was a topical editor of *Optics Letters* and is on the editorial board of *Journal of Nonlinear Optics* and *Photonics Science News*.

Bernard Kippelen is currently an *Assistant Research Professor* at the Optical Sciences Center of The University of Arizona. He got his Ph.D. is Nonlinear Optics from the University of Strasbourg in 1990. His current research interests include the study of functional nonlinear optical polymers for photonic applications. He is the co-author of over 80 publications in journals and conference proceedings, and of three book chapters on photorefractive polymers. He is a member of the Center for Advanced Multifunctional Nonlinear Optical Polymers and Molecular Assemblies (CAMP) funded by ONR where he works on electro-optic, photorefractive, and electroluminescent polymers. He is a Member of the Optical Society of America, the American Physical Society, and the American Association for the Advancement of Science.

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Profiles in Science

Alan MacDiarmid

Alan MacDiarmid is the Blanchard Professor of Chemistry at the University of Pennsylvania where he joined the faculty in 1955. For many years, he has been a principal investigator of the Office of Naval Research. He is sometimes referred to as "the father" of the science of conducting polymers, known usually as synthetic metals. He was the chemist responsible for the initial synthesis and chemical and electrochemical doping of polyacetylene, $(CH)_x$, the prototype conducting polymer, and the "rediscovery" of polyaniline, now the foremost industrial conducting polymer.

In 1973, he began research on $(SN)_x$, an unusual polymeric material with metallic conductivity. His interest in organic conducting polymers began in 1975 when he was introduced to a new form of polyacetylene by Dr. Hideki Shirakawa at the Tokyo Institute of Technology. The ensuing collaboration between MacDiarmid, Shirakawa and Alan Heeger (then at the Department of Physics at the University of Pennsylvania) led to the historic discovery of metallic conductivity in an organic polymer.

This discovery resulted from ONR funding. Continued ONR support allowed MacDiarmid and Shirakawa to attempt the first chemical doping of $(CH)_x$ and to collaborate on detailed physics studies with Heeger. These studies proved that an organic polymer could be readily doped to the metallic regime and introduced a phenomenon which was completely new and unexpected to both the chemistry and physics communities. This unleashed a floodgate of research world-wide in chemistry and physics concerning interrelationships between the chemistry, structure and electronic properties of semiconducting and metallic organic polymers which has continued to expand to this day.

Applications of these materials appear in such diverse areas as rechargeable batteries, electromagnetic interference shielding, anti-static dissipation, stealth applications, corrosion inhibition, flexible "plastic" transistors and electrodes, and electroluminescent polymer displays.

Professor MacDiarmid is the recipient of many honorary degrees and awards including: Chemical Pioneer Award of the American Institute of Chemists, the Francis J. Clamer Award of the Franklin Institute, Philadelphia, and "Top 100" Innovation Award from *Science Digest*. He is a Fellow of the American Institute of Chemists, published over 500 papers, and holds 20 patents.

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