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FINAL REPORT
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for period 16 January 1991 to 15 July 1991

ULTRAFAST PASSIVE SHIELDS FOR LASER AND BALLISTIC PROTECTION

Contract No. DAAL04-91-C-0019

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to

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"The views, opinions, and/or findings contained in this report are those of the author and should not be construed as an official Department of the Army position, policy, or decision, unless designated by other documentation."

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PROJECT SUMMARY

Addressing the need for laser eye protection in the Visible spectral region, the present work sought to demonstrate the applicability of a novel technology for dynamic, broad-band, ultrafast (sub-ns), passive laser shields based on conducting polymers (CPs) and inorganic semiconductor (SC) materials in a matrix to a wider range of SCs and CPs. Effective laser shielding was clearly demonstrated to occur for a number of varied systems, including Bi₂S₃ with poly(N-phenyl-2-naphthyl amine), poly(2-vinyl naphthalene), poly(9-vinyl carbazole), CdS with poly(2-naphthyl amine), Te with poly(N-phenyl-2-naphthyl amine) and others. The laser shielding was shown to be a cumulative effect of three complementary phenomena: the intrinsic nonlinear optical (NLO) effect in the CP, the intrinsic NLO effect in the SC, when present, and SC to CP charge transfer. Independent transient absorption (TA) studies showed switching to be broad-band, with risetimes in the sub-ns region, limited by instrumental measurement, and falltimes in the tens of ns. Laser shielding efficiency, characterized by $\Delta OD = OD(\text{under laser}) - OD(\text{rest})$, of greater than 1.0 at 532 nm were achieved for a number of systems at incident energies of ca. 0.25 mJ/pulse. Matrices of SCs and CPs in PVA and PEMA, and coatings on polycarbonate sheets and lenses and diamond-like-coated polycarbonate showed good laser shielding efficiency. The prognosis is for incorporation of the SCs and CPs exclusively into polycarbonate matrices or substrates for ballistic protection combined with laser shielding.

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A. BACKGROUND, FEATURES OF PROPOSED TECHNOLOGY
AND PROJECT OBJECTIVES

I. TECHNICAL BACKGROUND, FEATURES OF PROPOSED TECHNOLOGY

Need for laser protection

A strong and increasingly critical need exists for providing protection against accidental or deliberate exposure to hazardous laser radiation in the battlefield. This radiation emanates from use of target-designation or range-finding equipment, but may also emanate from hostile sources. Protection is primarily targeted at personnel eyes, and secondarily at sensitive sensors, in the 400 - 4,000 nm region, with the 700 - 4,000 nm region being protectible by static filters. The objective is to obtain a protective mechanism that is passive, i.e. not needing external activation, dynamic, i.e. switching from an inactive rests state, broad-band, and ultrafast, i.e. with a risetime in the sub-ns region. An additional objective is to have the protective mechanisms or substances incorporated into ballistic protective substances such as polycarbonates for ballistic as well as laser protection.

Specifications for laser protection

Specifications for protective devices generally require at least 50%, and preferably 75% scotopic and photopic transmission (i.e. OD's 0.3 and 0.15 respectively) in the unswitched, rest state, preferred laser-switched optical densities (ODs) of 4.0, non-distortion of incident light in the unswitched state, no angular dependence of the protective mechanism, and protection against both pulsed and CW lasers. At each wavelength, Maximum Permissible Exposures (MPEs) are defined for the human eyes or, in some cases, for sensitive sensors such as specialized TV cameras.

Basis of proposed technology

Addressing the above needs, the proposed technology had projected a novel approach, involving utilization of the inherent electrochromic properties of conducting polymers (CPs), which enable them to turn from broad-band transparent to opaque states (usually through transfer of charge from an electrode), in a novel manner. Inorganic semiconductor materials (SCs) were used which could be photoactivated by the laser in an ultrafast regime, and transfer charge directly to the CPs, causing them to switch electrochromically in an ultrafast regime. The unique feature of the technology is that the SC provides both the trigger and the energy for the laser-induced switching of the CP.

An additional feature of the proposed technology is that it represents the cumulative effect of three complementary phenomena: the intrinsic nonlinear optical (NLO) effect in the CP, the intrinsic NLO effect in the SC, and SC to CP charge transfer. Most CPs, and practically all those investigated in the present work, have broad-band electrochromic characteristics of the type illustrated in Fig. 1. Fig. 2 shows the basic steps in the laser-induced SC to CP charge transfer and their time regimes.

Advantages of proposed technology

Advantages of the technology over extant technologies such as dielectric filters, metalloporphyrin dyes, thermal (e.g. VO₂) devices, and nonlinear optical effect based devices include:

- o Lack of distortion of spectral distribution (implying that the relative intensities of the input wavelengths are approximately the same as those of the output wavelengths),
- o no angular dependence,
- o sub-ns switching risetimes,
- o no power requirements,
- o dynamic and passive operation,
- o tailorable, broad-band action, and
- o low cost, estimated to be in the \$100's/device.

II. PROJECT OBJECTIVES

Utilizing the technology outlined above, the present project sought to prove its viability and applicability for a range of semiconductor (SC) and conducting polymer (CP) combinations, and to demonstrate that high laser shielding efficiencies, characterized by changes in OD, could be achieved for samples with low rest-state (unswitched) ODs. A number of SCs and CPs were identified at the outset for the work. The specific technical objectives as identified in the Phase I proposal were:

1. Synthesize and characterize selected novel soluble conducting polymers based on trends identified in prior Gumbs work, with emphasis on matching to selected semiconductor materials, improved processibility and greater stability and order. Theoretical as well as experimental studies were to be used for the characterization.
2. Fabricate prototype SC/CP devices, normally on substrates such as glass (slides), glass lenses or polycarbonate slides, laminates or lenses, based on selection of matching SCs and CPs and other factors.
3. Test these with pulsed lasers to verify switching, and measure laser shielding efficiency as characterized by change in OD.
4. Conduct limited number of CW laser tests for a limited number of samples.

In accordance with the above objectives, the following tasks were identified for the Phase I work:

- Task 1: Synthesis, Characterization of Selected Additional Novel Soluble Conducting Polymers, Screening of Polymers
- Task 2: Prototype Device Fabrication, Extended Pulsed Laser Studies
- Task 3: CW Laser Studies

Task 4: Final Report

B. WORK CONDUCTED AND RESULTS

I. SCREENING OF POLYMERS

Theoretical Screening

As an integral part of the screening effort, theoretical (quantum chemical) calculations were conducted on existing and hypothetical polymer and monomer structures, employing semi-empirical, Extended Hueckel based band structure calculations. These were conducted by our full-time staff theoretical chemist, Dr. G.V. Kulkarni, employing adaptations of the band-structure program EHMACC with accompanying molecule-level calculations using MOPAC.

To start with, geometry optimizations were conducted on a number of monomers to make them suitable for input to the band-structure programs. These monomers included:

- o 3-amino pyrazole,
- o 1-amino pyrene,
- o diphenyl amine,
- o 4-amino biphenyl and
- o the amino quinolines.

It was found in comparative calculations on 3-amino pyrazole/pyrazole and 2-amino pyridine/pyridine that the amino group definitely contributes to lowering the band gap by breaking the aromatic ring electronic current and preferentially contributing to the extended chain electronic current. For instance, the HOMO-LUMO gap in pyrazole was found to be 9.816 eV whereas it was 8.522 eV in 3-amino pyrazole. A low HOMO-LUMO gap is indicative of a low polymer bandgap and thus more efficient CP switching in a SC/CP interface. Thus the strategy adopted in the present work of employing aromatic amines as monomer bases for electropolymerization was validated. Table I shows HOMOs, LUMOs and HOMO-LUMO (H-L) gaps for selected monomers.

TABLE I: HOMOs, LUMOs and HOMO-LUMO (H-L) gaps for selected monomers, computed through MOPAC optimization.

<u>Monomer</u>	<u>HOMO (eV)</u>	<u>LUMO (eV)</u>	<u>H-L gap</u>
Imidazole	-9.436	0.634	10.070
2-amino-	-8.118	0.994	9.112
4-amino-	-7.806	0.870	8.676
Thiazole	-10.045	-0.653	9.392
4-amino-	-8.372	-0.380	7.992
Thiadiazole	-10.683	-1.133	9.550
2-amino-	-9.202	-0.773	8.428

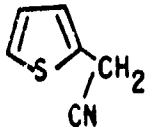
The compatibility of the SC and CP and the laser shielding efficiency of the CP/SC interface is directly dependent on the band gap of the CP. Again, a low band gap (\sim H-L gap) indicates a polymer with better potential laser shielding capability.

Based on the extensive theoretical calculations, a number of monomers were identified that would yield polymers with promising optical and other properties relevant to laser shielding. These included transparency in the de-doped state and chemical and thermal stability (for instance based on blocking of active reactive or crosslinking sites in the polymer chain). These monomers included:

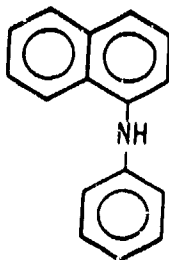
o 6-amino quinoline
o 2-amino benzimidazole

o 8-amino quinoline
o 4-amino quinaldine

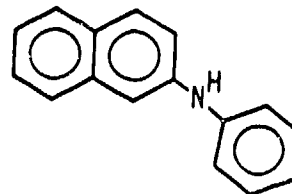
cyano-2-methyl
thiophene (1)



N-phenyl, 1-naphthyl
amine (2)



N-phenyl 2-naphthyl amine
(3)



The potential poly(2-cyano-methyl thiophene) (polymer of 1) constituted a 'self-doped' conducting polymer. N-phenyl-1-naphthyl amine (2) did not electropolymerize but N-phenyl-2-naphthyl amine (3) yielded an electropolymer with exceptional optical, stability and laser shielding properties, as described below. While it is possible that poly(1) may release a toxic gas when heated, the toxicity of each monomer will be first tested before any attempts at electropolymerization. The toxicity of materials is discussed in a subsequent subsection in the sequel.

In addition to the above, band-structure diagrams (including density of states) computed by the program EHMACC were plotted for several existing and hypothetical polymers. These yielded additional detailed information on bandgaps, and band structures at zone centers and edges, useful for predicting the rest-state and excited-state optical properties of the polymers.

Electropolymerizations, electrochemical, optical screening

A number of monomers were identified for polymerization based on the prior work as well as the theoretical screening. Their electrochemical polymerizations were investigated with the dopants tetrafluoroborate and tosylate in

acetonitrile, propylene carbonate and benzonitrile media, in a 3-electrode as well as two-electrode mode, the latter with pyrolytic graphite counter and pyrolytic graphite or ITO working electrodes. In the 3-electrode mode, the polymerization onset was studied, while in the 2-electrode mode, applied potentials ranging from +2.1 V to +10.0 V were investigated.

After the electropolymerization was proven successful, polymer films were characterized for electrochemical (e.g. by cyclic voltammetry), spectro-electrochemical, optical (FTIR, NMR, UV-Vis-NIR) and stability properties. The polymers were synthesized in bulk and their conductivity, solubility and solution optical properties evaluated. From the electrochemical redox potentials, the compatibility of the polymers with the bandgaps and band structures of various semiconductors was determinable. From the spectro-electrochemical properties, the OD contrast between switched and unswitched states, and thus the laser shielding efficiency, was determinable.

We also investigated purely chemical polymerization methods in order to arrive at an alternative method for bulk-scale production of CPs. As an example of the chemical method, an aromatic amine is allowed to polymerize at 0 - 3 °C in 1 M aqueous HCl containing an oxidizing agent such as ammonium persulfate. Experiments with 3-aminoquinoline indicated a rapid generation of radical cations which reacted with monomer to yield other radical cations, propagating the species. The chain was terminated by coupling or by chain transfer. At the end of the reaction, the mixture was neutralized with 1 M ammonium hydroxide, precipitating the reduced form of the polymer.

In comparison to electrochemical polymerizations, chemical polymerizations gave significantly larger yields (up to 10 times by weight), and usually higher conductivities (normally in the 1 S/cm region) and higher MWt. However, the polymers also appeared to degrade faster, being dedopable in solution. These problems for chemical polymerization can be overcome in future work.

II. NEW POLYMER SYNTHESSES AND THEIR PROPERTIES

The properties of a number of the new polymers synthesized during this period were evaluated. Table II lists structures of monomers yielding successful and promising new CPs, while Table III lists salient properties of a number of these.

Fig. 3 shows the characterization cyclic voltammogram for poly(3-amino pyrazole), while Figs. 4,5 show those for poly(2-amino pyridine) and poly(1-amino pyrene) respectively. Stability and conductivity studies of poly(3-amino pyrazole) indicated that it had exceptional environmental stability and thus would be very durable when incorporated into SC/CP interfaces.

In addition to the above polymers, poly(1-amino anthracene) and poly(4-amino quinaldine) (structures given following Table II below) yielded polymers with high transparency in their unswitched states in the 400 - 700 nm region together with predicted acceptable switched/unswitched OD contrast ratios. Preliminary laser tests at 0.1 mJ/pulse incident energy indicate ΔOD 's in the 0.95 region.

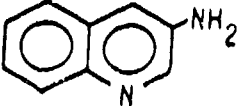
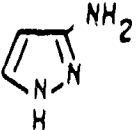
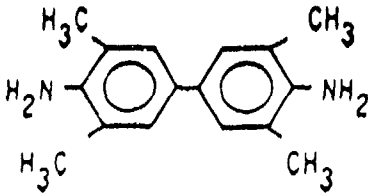
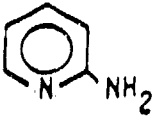
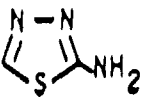
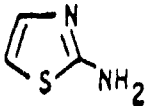

Additionally, poly(N-phenyl-2-naphthyl amine), whose monomer structure has been given above (3), proved to be an exceptionally versatile polymer showing very high solubility and stability in addition to high laser shielding efficiencies as shown in the results subsequently. At +5.35 V with 0.2 M monomer in 0.15 M $\text{Et}_4\text{NBF}_4/\text{CH}_3\text{CN}$ a light yellow-green polymer with indicated doping level of ca. 3% was obtained, which was nearly 50-75% miscible with organic solvents such as DMF.

Toxicity of monomers, SCs and CPs used

Almost all monomers used are obtained from commercial vendors who supply Materials Safety Data sheets. These indicate that the monomers can be handled with standard chemical safety handling techniques. Generally when the monomers are polymerized, their active sites, responsible for their toxicities, are incorporated into the polymer chain and thus eliminated. Residual monomers present in polymers are discounted as the polymers are thoroughly washed before sample preparation.

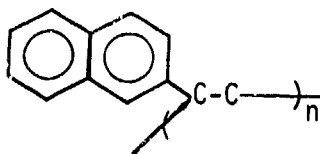
The SCs also have some toxicities (especially the Cd based SCs). These can generally be discounted because of the unique sample preparation methodology used, i.e. encapsulation into a PEMA or polycarbonate matrix. In future work, e.g. in Phase II, additional methods for toxicity control will be developed to prevent toxic exposure during ballistic rupture or extended laser heating.

TABLE II: Structures of monomers yielding successful and promising conducting polymers (CPs), together with abbreviations and salient properties.

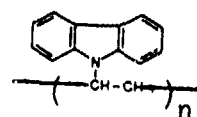
<u>Monomer</u>	<u>Structure</u>	<u>Dopants, Potentials Yielding Successful Polymerizations</u>
3-amino quinoline (3AQ)		BF_4^- : +2.5V, +3.6V, +5.25 V tosylate: +3.6 V
3-amino pyrazole (3APaZ)		BF_4^- : +3.6 V; +5.2 V
3,3',5,5' Me ₄ benzidine (3355MeBz)		BF_4^- : +2.6 V; +5.2 V tosylate: +2.5 V ClO_4^- : +2.5 V
2-amino pyridine (2APy)		BF_4^- : +5.2 V
2-amino-1,3,4-thiadiazole (2A134TDAz)		BF_4^- : +5.2 V; tosylate: +3.6 V
2-amino thiazole (2ATaZ)		BF_4^- : +5.2 V tosylate: +3.25 V
Poly(1-amino pyrene) (P(1APyre))		

(Table II, cont.): Additional Structures of Polymers:

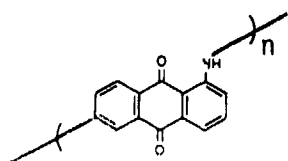
poly(2-vinyl naphthalene)



poly(9-vinyl carbazole)



poly(1-amino anthraquinone)



poly(4-amino quinaldine)

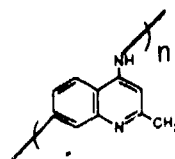


TABLE III: Additional salient properties of new polymers synthesized. For abbreviations used, see Table II.

<u>Polymer</u>	<u>Conductivity (S/cm)</u>	<u>Solubility (w/w)</u>
P3AQ	360	this polymer nearly 100% soluble in DMF, forming emulsion.
P(3APaZ)	315	9.5%
P(3355MeBz)	5.0 to 10.0	1.4%
P(2APy)	265	8.9%
P(2A134TDAz)	70	4.5%
P(2ATaZ)	70	7.9%

Other conducting polymers

Poly(diphenyl amine), another versatile polymer for laser shielding, was characterized from a number of different polymerization conditions (including chemical polymerization), variable doping, and other factors. Based on these results, we developed the capability to electrosynthesize and chemically synthesize polymer of desired doping level, chain length and other variables.

Additionally, two commercially available, highly transparent polymers, poly(9-vinyl carbazole) and poly(2-vinyl naphthalene) were found to be readily electrochemically dopable for incorporation into SC/CP interfaces. The advantages of these polymers were that they were highly soluble, and had near glass-clear transparency in their slightly doped or undoped states. Poly(3-amino quinoline), a polymer found versatile in earlier studies, was also tested in this project.

Spectroelectrochemical properties

An imperative property of CPs usable for laser shielding is high optical contrast between switched (doped) and unswitched (undoped) states. A large number of the polymers studied had exceptional OD contrasts between these states. Fig. 6 shows the spectroelectrochemical characterization curve for poly(3-amino quinoline), while Figs. 7, 8 show those for poly(2-amino pyridine) and poly(1-amino pyrene) respectively. Clearly, the first two polymers have exceptional OD contrasts, the switched/unswitched OD ratio being e.g ca. 120.0 for poly(2-amino pyridine) at 700 nm.

Polymer processibility

Table III shows that many of the polymers are highly soluble in common organic media, a property that makes them eminently processible. This property is especially useful for facility in fabrication of SC/CP interfaces, allowing for the SC-CP combinations to be processed in different ways such as in the form of slurries.

Additionally, during this work ball-milling of CPs, with or without SCs, was used to generate fine-particulate CPs for SC/CP interfaces. A jar mill and poly(ethyl methacrylate) (PEMA) in toluene, xylenes, or in some cases, DMF, were used. Finer-particulate CPs were found to generally have higher laser shielding efficiency. The ball-milled slurries could be spin-coated onto substrates for more uniform, optically homogeneous films.

III. SCREENING OF SEMICONDUCTORS (SCs)

As proposed in the Phase I proposal, at the outset of the project, the SCs were deposited as thin films on glass substrates by vacuum thermal evaporative deposition on which the conducting polymers (CPs) were subsequently deposited, forming the SC/CP interface. Our initial SC thin film deposition studies were conducted in the laboratory of Prof. R. Bartynski, Dept. of Physics and Astronomy, Rutgers University, Piscataway, NJ, via funding of

graduate student Alex See and on a Denton Vacuum Model 502A thermal evaporative deposition apparatus purchased by Gumbs. The objective was to obtain well-adhering SC films on glass with thicknesses less than 100 nm and optical densities (ODs) at 532 nm of less than 0.4. The films should also have had a fairly well-defined band edge. Such films would be suitable for incorporation into superior SC/CP interfaces. The following SC films were successfully deposited (bandgaps in parentheses):

- o CdSe (1.77 eV)
- o CdTe (1.44 eV)
- o ZnSe (1.7 eV)
- o Se (0.7 eV)

For a number of these SCs, the films had to be annealed after thermal evaporative deposition in order to produce sharply defined band edges, necessary for inclusion in SC/CP interfaces. Characterization UV-Vis spectra for a number of these SCs showed acceptable ODs, well-defined band edges.

However, in initial studies, all such films were found to ablate seriously at even moderate laser intensities. To prevent this, it was attempted to coat the SC thin films with a protective layer of the inert, transparent polymer poly(ethyl methacrylate) (PEMA). The CPs could themselves be incorporated into a PEMA slurry and coated on the thin film SCs. In first tests of this sample configuration, Se/glass and CdSe/glass electrodes were coated with 30% w/w PEMA/toluene (which contained a very dilute concentration, less than 1%, of chemically polymerized P(DPA)) as a binder, and these were tested for ablation (i.e. laser damage threshold) limits. Table IV below summarizes these results which are all for tests in the absence of an iris .

Subsequent to these tests, it was found that fine-particulate semiconductors could be used in the form of a ball-milled or simply mixed slurry in PEMA/toluene or PEMA/xylene media. The SC slurries could be incorporated with similar fine-particulate CP slurries to form the SC/CP interface. The SCs used in this second configuration, together with their bandgaps and the pre-ball-milled mesh size, are given below (Table IV). In particular, the new SC Bi_2S_3 was found to be extremely promising in laser shielding results.

TABLE IVA: Semiconductors (SCs) in fine-particulate, slurry-based configuration which yielded the most promising laser shielding efficiencies (bandgaps, mesh sizes in parentheses).

- Se (0.7 eV, -200 mesh)
- CdS (2.42 eV, 50 μ)
- Te (0.4 eV, -120 mesh)
- Bi_2S_3 (1.3 eV, -200 mesh)

TABLE IVB: Thin film (vacuum deposited) SC films tested with an inert encapsulant (protective) layer of poly(ethyl methacrylate) (PEMA) (see Table VI for test results).

Se, OD 0.62	CdSe, OD 0.48
Se, OD 0.65	CdSe, OD 0.62

IV. PULSED LASER TESTING

IV.1 Methodology

Two modes of testing under pulsed laser irradiation were employed in this project.

The first, conducted at the Regional Laser & Biotechnology Laboratory (RLBL), U. of PA, involved ns-regime transient absorption (TA) measurements. A Nd:YAG laser at 1064, 532 or 355 nm, 10 Hz, ca. 7 mm dia., 8 ns duration, energy 0.08 - 2 mJ per pulse, was used as the pump beam at 45° to the sample, and a Xe flash lamp, at 90° to the laser and 45° to the sample, as the probe beam for the region 370 nm to 800 nm. The probe could be monitored at delay times between nominal 0 ns and several μ s. Each experiment consisted of 100 averaged shots, ensuring that systems studied were highly reversible. These TA measurements yielded: a) the broad-band nature of the transient laser shielding capacity of samples and b) the risetime and falltimes of the samples. Fig. 9 summarizes schematically the TA arrangement.

In the second method, conducted with our in-house Nd:YAG laser at 532 nm (laser dia. 7 mm, pulsewidth 2.5 ns, 10 Hz, energies as below) was used in a manner yielding direct, cumulative laser shielding efficiencies for samples. Fig. 10 shows a schematic of the apparatus used. The rest-state (i.e. unswitched) OD, OD(rest), of the samples at 532 nm was first measured. Subsequently, the laser energy was set at the desired incident energy without any sample, I_0 . The following energies were used for laser shielding tests:

- o 50, 100, 250 and 500 μ J/pulse
- o 1.0, 2.5, 5.0 mJ/pulse.

The following energies were used for the preliminary laser damage threshold tests:

- o 2.5, 5.0, 10.0, 100.0 mJ/pulse.

Subsequently, the sample was placed in the beam path and the transmitted laser energy, I , was measured at the power meter. This yielded the laser-induced OD, $-\log_{10}\{I_0/I\}$. The laser shielding efficiency was then characterized by:

$$\Delta OD = OD(\text{laser}) - OD(\text{rest}) \quad \dots (1)$$

The sample-detector distance was generally maintained at 25", and an iris of 3 mm dia., emulating a photopic pupil, was placed directly in front of the detector. This method yielded the cumulative laser shielding efficiency over the fs - μ s regime, but did not yield rise- or fall- times or broad-band nature, which was revealed by TA studies.

IV.2 Sample preparation, samples tested

SC/CP combinations yielding optimal results

A large number of semiconductors (SCs) were tested, including:

- o Se, CdSe, ZnSe, CdTe, CdS, Te, Bi₂S₃.

A large number of conducting polymers (CPs) were tested, including

- o poly(diphenyl amine) (P(DPA)), poly(3-amino quinoline) (P(3AQ)),
- o poly(9-vinyl carbazole) P(9vinCz)), poly(2-vinyl naphthalene) (P(2-vin-Na),
- o and the new CP poly(N-Phenyl-2-naphthyl amine) (PNPhe2NA).

Of these those combinations yielding the best results are listed in Table V.

TABLE V: SC/CP combinations yielding best laser shielding results.

Se/poly(9-vinyl carbazole) (P(9-vin-Cz))
Se/poly(2-vinyl naphthalene) (P(2-vin-Na))

CdS/P(2-vin-Na)

Te/poly(N-phenyl-2-naphthyl-amine) (P(NPhe2NA))

Bi₂S₃/P(NPhe2NA)
Bi₂S₃/P(2-vin-Na)
Bi₂S₃/P(DPA)

First configuration- thin film SCs

As mentioned above, at the outset of the project, SC thin films were fabricated by vacuum thermal evaporation, with the CPs being deposited on these either from solutions or from slurries containing transparent encapsulants such as PEMA. Although tests with PEMA-encapsulated SC-only films showed that laser ablation was substantially reduced, it was not entirely eliminated and was continually found to be a problem. Thus an alternative sample configuration as described below was used.

Second configuration- films deposited from slurries of CPs/SCs

Fine-particulate SCs were procured commercially and fine particulate CPs prepared, and slurry suspensions of these were prepared for film deposition. The following sample preparation methods were used:

- 1) Mixing of slurry suspension of SC in toluene/PEMA and CP solution in DMF and drop- or dip-coating.
- 2) Ball-milling of SC and CP separately and then mixing resultant slurries and drop- or dip- coating.

- 3) Co-ball-milling of SC/CP together in 1:1 proportion.
- 4) Spin-coated modifications of the above methods.

The medium for ball milling and for slurry suspension was a ca. 10% - 30% solution of the transparent, inert polymer poly(ethyl methacrylate) (PEMA) in toluene. Ball milling was done in our newly acquired jar ball mill and spin coating on our newly acquired Integrated Technologies spin coater. Substrates were microscope glass slides (1" X 3").

As far as possible, it was attempted to test samples with rest state OD of 0.45 or less (transmission 35% or more) (at the 532 nm test wavelength).

For the first method, using DMF, the SC or CP were prepared as slurries through thorough mixing in media which included toluene or xylene as support solvent and poly(ethyl methacrylate) (PEMA) or poly(acrylonitrile) (PAN) as inert, transparent polymer matrices which when dried yielded clear films in which the SC or CP were impregnated. In cases, the polymer was mixed into the slurry as a concentrated DMF solution to aid in dissolution. The sample films were then cast as thin films on glass slides. The SCs were generally commercially available as fine-particulate materials (ca. 3 μm). The CPs and coarse SCs were ground with mortar and pestle. The ODs used for these samples were attempted to be limited to no more than 0.5, and if possible less than 0.3.

In actual laser results, it was found that co-ball-milling of SC-CP in 1:1 ratio yielded the best results, while spin-coated samples did not have appreciably higher laser shielding than non-spin-coated samples.

IV.3 Thin-film SC configuration and Transient Absorption results

Transient Absorption (TA) results

In TA measurements, the following CPs/SCs yielded the best results:

poly(diphenyl amine) (Poly(DPA)); poly(3-amino quinoline) (Poly(3AQ))

CdSe; Se.

Figs. 11A-E show TA spectra for the Se/Poly(DPA) (SC/CP) combination. Figs. 11A and 11B show reference spectra for SC and CP only, while Figs. 11C-E show TA spectra at 20, 40 and 100 ns monitoring time delays. The TA for this SC/CP combination is extremely broad band, and rises over 20 ns (C) to peak at ca. 60 ns (D), commencing to fall at 100 ns (E). Figs. 12A shows reference spectra for poly(3AQ) only, while Figs. 12B-D show TA spectra at 20, 60 and 100 ns respectively for the Se/poly(3AQ) SC-CP combination, again showing a broad band, long-lived transient. The relatively small ΔOD 's obtained (ca. 0.15) are a product of the sample construction, and can be significantly enhanced (over one order of magnitude) employing fine-particulate SC-CP combinations (see below). All the above samples were slurry suspensions.

Results for solid state CdSe/poly(DPA) SC/CP interfaces were also encouraging, with ΔOD 's in the 0.04 range being achieved.

Broad-band nature and sub-ns risetime of laser shielding

Several important features are apparent in these results. Firstly, the TA, and hence the potential laser shielding, is extremely broad-band, across practically the entire visible spectral region. Secondly, the risetime is instantaneous within instrumental limitations, i.e. it is smaller than ca. 1 ns. Thirdly, the falltimes are in the tens of ns, which again augurs well for laser shielding, since it indicates that the systems will remain in a laser shielding state for that time. Finally, the laser shielding magnitudes, as indicated by Δ (Absorbances), are small only because the concentrations of SC and CP used in the slurries to generate observable results are very small and the laser pump energies are also small.

Results of samples of first, thin-film SC configuration

In first tests of the first, thin-film SC configuration, Se/glass and CdSe/glass electrodes were coated with 30% w/w PEMA/toluene (which contained a very dilute concentration, less than 1%, of chemically polymerized P(DPA)) as a binder, and these were tested for ablation (i.e. laser damage threshold) limits. Table VI summarizes these results which are all for tests in the absence of an iris. It is seen that all of the samples ablate in presence of the PEMA protective binder.

TABLE VI: Laser damage (ablation) thresholds for thin-film SC's coated with a protective layer, ca. 0.1 mm, of PEMA (containing some P(DPA)).

Sample	DAMAGE AT (mJ/pulse)				
	0.1	0.25	0.5	1.0	2.5
Se, OD 0.62	No	No	No	Yes, sign.	"
Se, OD 0.65	No	No	No	Yes, sign.	"
CdSe, OD 0.48	No	No	No	Yes, some	sign.
CdSe, OD 0.62	No	No	No	Yes, some	sign.

IV.4 Detailed In-house pulsed laser results

Fig. 13 summarizes results for a set of experiments employing thin-film Se/glass as the SC and poly(9-vinyl carbazole) and poly(2-vinyl naphthalene) as the polymers. Since the polymers were cast onto the SC thin-film from PEMA/toluene slurries, protection of the Se film from ablation, as for the samples of Table I, was inherently provided. The following are observable from Fig. 13: a) Poly(9-vinyl carbazole) on its own shows significant laser shielding capability, ascribable to third-order nonlinear optical (NLO) effects, whereas poly(2-vinyl naphthalene) does not; b) The laser shielding capability of the poly(vinyl carbazole) is greatly enhanced when incorporated into a SC/CP interface with Se; c) The laser shielding capability of poly(2-

vinyl naphthalene) is enhanced when incorporated into a SC/CP interface with Se, but to a much smaller extent. Thus it would appear that the SC/CP combination Se/poly(9-vinyl carbazole) is a good candidate for optimization of laser shielding efficiency. It must be borne in mind that both polymers were undoped, and it is possible that doping, e.g. of poly(2-vinyl naphthalene), will yield a better laser shielding efficiency. This will be evaluated in the subsequent period.

Fig. 14 shows laser shielding results for the SC/CP combination CdS/poly(2-vinyl naphthalene). CdS is a large-bandgap (2.24 eV) SC, and would not in its pure state be expected to be activated at the laser excitation wavelength used. The polymer used is entirely undoped again. The observed laser shielding thus may possibly be ascribed to impurities in CdS causing a lowering of bandgap and thus laser excitation, coupled with intrinsic third-order NLO effects in both SC (major) and polymer (minor).

Fig. 15 shows laser shielding efficiency for the SC Te, the newly electro-synthesized CP poly(N-phenyl-2-naphthyl amine) (P(NPhe2NA)) (in its very lightly doped form) and for this SC/CP combination. The laser shielding capacities of the SC and CP alone are negligible (ΔOD ca. 0.08 max.), whereas that for the SC/CP combination is appreciable (ΔOD ca. 0.46), thus implying that laser-induced SC \rightarrow CP charge transfer is occurring in this system, though to a nominal degree.

An additional feature evident in all of the above results is that the laser shielding efficiency appears to actually drop for intensities higher than ca. 1.0 mJ/pulse, which again is ascribed to sample ablation at these intensities.

Results with the new SC Bi_2S_3

Figs. 16-21 summarize laser shielding efficiencies as characterized by ΔOD 's for the Bi_2S_3 -based SC/CP combinations. In Fig. 16, employing poly(N-phenyl-2-naphthyl-amine) (P(NPhe2NA)) as the CP, the data for SC-only and CP only show that the SC/CP combination has a cumulative shielding larger than the sum of its parts, pointing to laser induced SC to CP charge transfer. This is substantiated by the fact that the highest shielding is obtained for the SC:CP= 1:1 proportion. This is true for the poly(2-vinyl naphthalene) (P(2VinNa)) - Bi_2S_3 combination as well (Fig. 17). It is to be noted that this polymer is an extremely transparent polymer in its rest, undoped state as used in the SC-CP interface.

The Bi_2S_3 -poly(diphenyl amine) (P(DPA)) combination (Figs. 18-21) appears to be especially promising, with ΔOD s as high as 1.5 being achieved. There is a decrease in shielding at higher energies, which we have determined to be due to thermal ablation of the retained solvent in the PEMA matrix. This is a problem that will be solved with improved sample fabrication, which we are currently working on. Again for this SC/CP combination, there is clear evidence for laser-induced SC \rightarrow CP charge transfer, i.e. laser and SC-induced switching of the conducting polymer, the basis of the proposed technology.

Figs. 20-21 show shielding data for the same SC/CP combination, but with variation of polymer concentration instead of SC concentration. Fig. shows data for another SC/CP combination, Bi_2S_3 /poly(9-vinyl carbazole) (P9VinCz). This has relatively poor shielding and moreover shows very significant ablation even at incident laser energies as low as 2.5 mJ/pulse.

All of the above data show very significant laser shielding efficiencies, ΔODs being in the 1.5 range, and total, switched ODs being above 2.0.

Clear evidence for laser-induced SC--->CP charge transfer

All of the above data also show clear evidence of laser-induced SC--->CP charge transfer, i.e. laser-activated, SC-induced switching of the conducting polymer, which was sought to be demonstrated in the proposed technology. Thus the feasibility of the technology appears to have been clearly substantiated for new SC/CP combinations in this period.

Reproducibility of laser shielding

The reproducibility of the results at high incident laser energies, greater than 1.0 mJ/pulse was within 5% in all cases, except when degradation of the same sample over a period of several weeks was involved, in which case it was within 25%. Reproducibility at lower energies, e.g. 0.1 mJ/pulse and 0.25 mJ/pulse, was within 15% for duplicate samples, to ca. 35% for the same sample degraded over several weeks.

Table VII below summarizes the best pulsed laser results obtained in the present project.

TABLE VII: Summarial pulsed laser shielding results. Values are for 0.25 mJ/pulse incident laser energy. The ΔOD values are averages over ca. 10 measurements. The doping level of the polymer and the sample film thickness are indicated in parentheses.

<u>System</u>	<u>Typical ΔOD</u>
Se/poly(9-vinyl carbazole) (P(9-vin-Cz)) (0.5%, 0.1 mm)	1.4
Se/poly(2-vinyl naphthalene) (P(2-vin-Na)) (0.5%, 0.1 mm)	0.5
CdS/P(2-vin-Na) (0.5%, 0.1 mm)	0.94
Te/poly(N-phenyl-2-naphthyl-amine) (P(NPhe2NA)) (1.5%, ca. 20 μM)	0.47
Bi_2S_3 /P(NPhe2NA) (1.5%, ca. 20 μM)	1.1
Bi_2S_3 /P(2-vin-Na) (1.5%, ca. 20 μM)	1.2
Bi_2S_3 /P(DPA) (1.5%, ca. 20 μM)	1.4

V. CW LASER RESULTS

Two methodologies were used for the CW laser studies. In the first, a pump and probe method very similar to the TA studies at RLBL was used, with the probe being a monochromatized beam (at 532 nm) at right angles to the laser pump beam and at 45° to the sample. The second method was identical to the in-house pulsed laser test setup, with the laser functioning as both pump and probe. In this, integration times for each experiment of 5.0 to 60.0 sec. were used.

Due to resource limitations, only a few, Bi_2S_3 -based systems were tested. Those with the polymers poly(N-phenyl-2-naphthyl amine) and poly(2-vinyl naphthalene) showed significant laser shielding (ΔOD ca. 0.1 to 0.3) for results integrated over several minutes.

VI. PRELIMINARY THRESHOLD, BALLISTIC PROTECTION RESULTS

Selected laser damage threshold studies have been summarized in Table VI above for thin-film SC based samples.

For provision of ballistic protection, the most likely configuration to be used adopting the present technology would be use of polycarbonate substrates as the base, anti-ballistic material. The configuration would either have coatings of SC/CP on polycarbonate, or would somehow incorporate polycarbonate and SC-CP into a matrix which could be moulded by compression, heat or a combination. Polycarbonate is known to be the best material to date for ballistic protection.

In the present project, detailed testing of the first configuration was conducted in the final monthly reporting period. For the second configuration, the CALIBRE brand granular polycarbonate was ordered from Dow Chemical but was not received in time for the tests. For the first configuration, coatings on polycarbonate sheets and lenses and diamond-like-coated polycarbonate showed good laser shielding efficiency (in the 0.7 - 1.3 region for non-spin-coated samples) combined with fair adhesion. Laser tested samples were sent to the contract monitor as deliverables, as requested.

FACTORS INFLUENCING LASER SHIELDING

From the Phase I work, it was discerned that the following factors appear to clearly and directly affect the laser shielding:

- o Identity of individual SC, CP (i.e. SC-CP match);
- o SC:CP proportion, with 1:1 molar ratios yielding the best results;
- o Doping level, with lower doping levels giving better results as expected

It is of course planned that other variables influencing laser shielding will be identified in future work, e.g. in Phase II. Some of these variables can be tentatively identified as:

- o dopant type;
- o polymer conductivity;
- o SC purity, doping, and particle size;
- o sample preparation/processing method.

At this point, the possible scientific limitations of the technology can be identified as follows:

- o crystallinity or amorphous nature of the SC;
- o enhanced or decreased recombination effects (hole-electron) in the SC;
- o control over morphology of CP.

C. SUMMARIAL RESULTS AND ESTIMATES OF FEASIBILITY

Conclusions From Phase I Work

The following could be concluded from the Phase I work:

- o The viability of the technology was clearly demonstrated as applied to a variety of different SC/CP systems with the semiconductors (SCs) Se, CdS, Te, Bi₂S₃, and the conducting polymers (CPs) poly(diphenyl amine), poly(3-amino quinoline), poly(9-vinyl carbazole), poly(2-vinyl naphthalene), poly(N-phenyl-2-naphthyl amine).
- o Several especially transparent polymers, e.g. poly(9-vinyl carbazole) and poly(2-vinyl naphthalene) were found effective in SC/CP interface laser switching. Many other SC/CP systems studied had rest-state (unswitched) ODs at 532 nm of less than 0.3, i.e. transmissions greater than 50%.
- o Switching was shown to occur in all cases with risetimes in the sub-ns region, limited by instrumental measurement, and falltimes in the tens of ns.
- o Laser shielding efficiencies, as characterized by ΔOD 's, in the region of 1.5, and total switched ODs in the region of 2.0 were achieved for a number of systems.
- o Charge transfer, SC to CP, was clearly demonstrated to occur with reference SC-only and CP-only laser experiments.
- o Pulsed laser switching thresholds as low as 0.1 mJ/pulse (5 ns pulse, 7 mm dia.) were demonstrated.
- o A large number of novel conducting polymers were synthesized. All of these were highly soluble, and hence eminently processable, important for ease of fabrication of any ultimate devices. Reprocessed films were as electroactive as virgin films.
- o Many new polymers were found to have extremely broad-band absorptions, useful for broad-band laser filters.
- o It was determined that the actual laser shielding was a combination of three complementary effects, viz. a) SC to CP charge transfer, b) intrinsic 3rd order nonlinear optical (NLO) effect in SC, c) intrinsic 3rd order NLO effect in CP.

Advantages of proposed technology

The advantages of the present SC/CP interface technology can be summarized as follows:

- o *Dynamic* (switchable), *broad-band* (near-UV-Visible-NIR), *ultrafast* (sub-ns), *passive* action.
- o More transparent polymers affording high unswitched (rest) state transmissions, ca. 50 - 75% scotopic.
- o Laser shielding efficiencies, characterized by Optical Density (OD) changes, Δ ODs, appear to be high, demonstrated in Phase I to be greater than 1.2 for many systems. When optimized, these values may be substantially higher. Total switched ODs near 2.0 were demonstrated.
- o The laser shielding is a cumulative effect of three reinforcing phenomena: SC to CP charge transfer and the intrinsic NLO effects of the CPs as well as of the SC where applicable.
- o There is no distortion of spectral distribution.
- o There is no angular dependence of the laser shielding.
- o There is less bulk as compared e.g. to optical notch devices.
- o There are no power requirements.
- o Cost is reasonable, estimated to be in the \$100's per device.

These advantages are over alternative technologies such as: a) absorbing dyes (e.g. porphyrins), suffering from low transmission; b) reflective (mainly optical notch) filters, suffering from broad-band coverage and/or poor transmission and angular dependence; holographic filters based on diffraction; reflective dielectric filters based on interference; rugates based on diffraction; liquid crystals; c) NLO-effect based devices, suffering from low macroscopic nonlinear susceptibilities; d) ferroelectric liquid crystals, suffering from slow switching rates, non-passive action; e) thermal based, e.g. VO₂-based, devices, suffering from non-passive and slow action; f) static filters, inapplicable to broad-band coverage; g) CPs switched electrochemically, suffering from slow switching rates.

Estimates of Feasibility

The feasibility of constructing passive, broad-band, dynamic, ultrafast (sub-ns) laser shielding devices based on SC/CP interfaces was clearly demonstrated in this project. The viability of the technology was demonstrated with very varied SCs and CPs and their combinations. The targets of at least 50% rest state scotopic transmission and switched ODs near 2.0 were achieved or exceeded. Switching risetimes were shown to be ultrafast, in the sub-ns range. Rise times were shown to be in the tens of ns.

D. TASK SCHEDULING OUTLINE

(- - - planned; _____ achieved)

TASK	MONTH	1	2	3	4	5	6
1. CP syntheses, screening		-	-	-	-	-	-
2. Device fabricn., pulsed laser studies		_____	-	-	-	-	-
3. CW laser studies			_____	_____	_____	-	-
4. Final report						_____	-

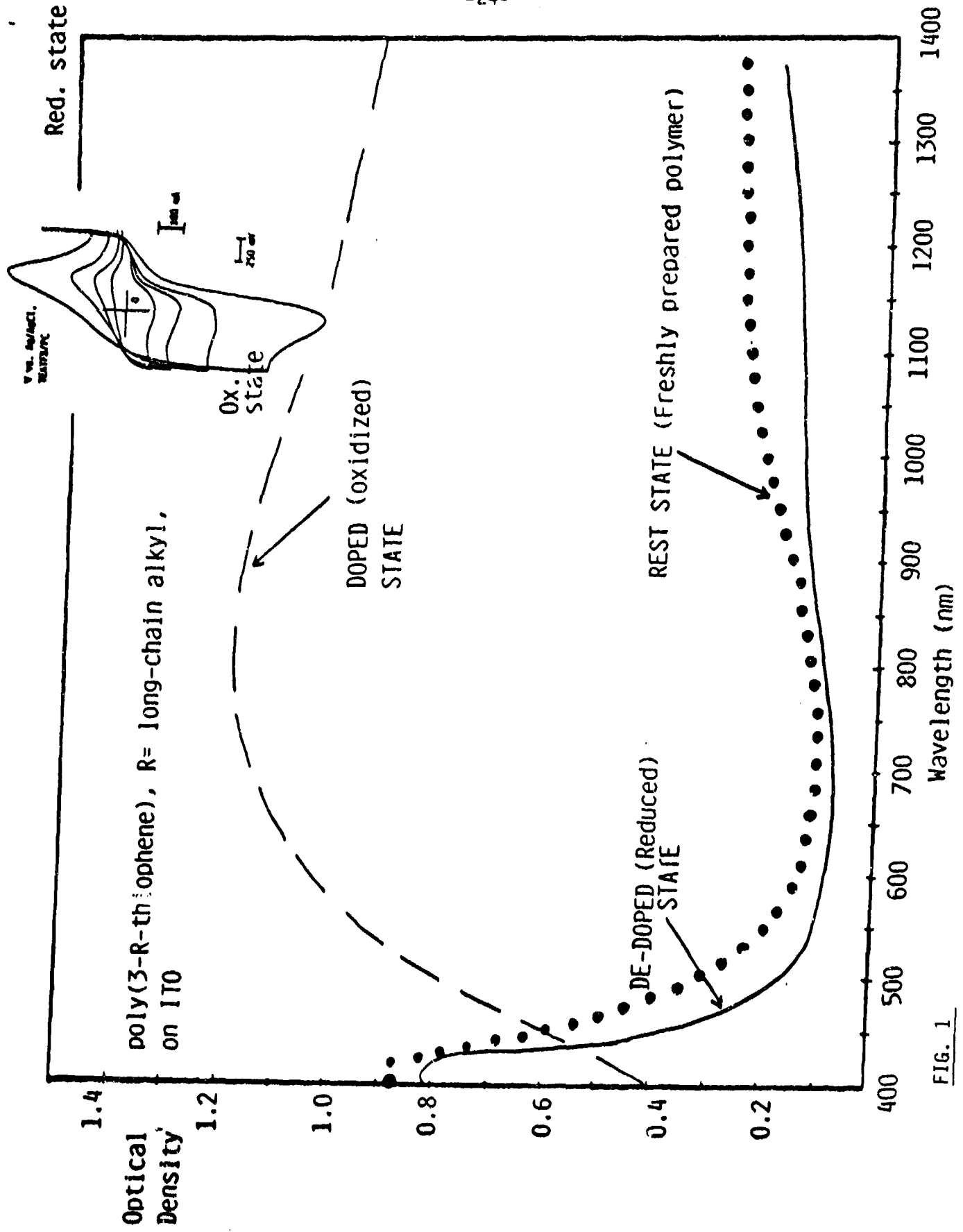
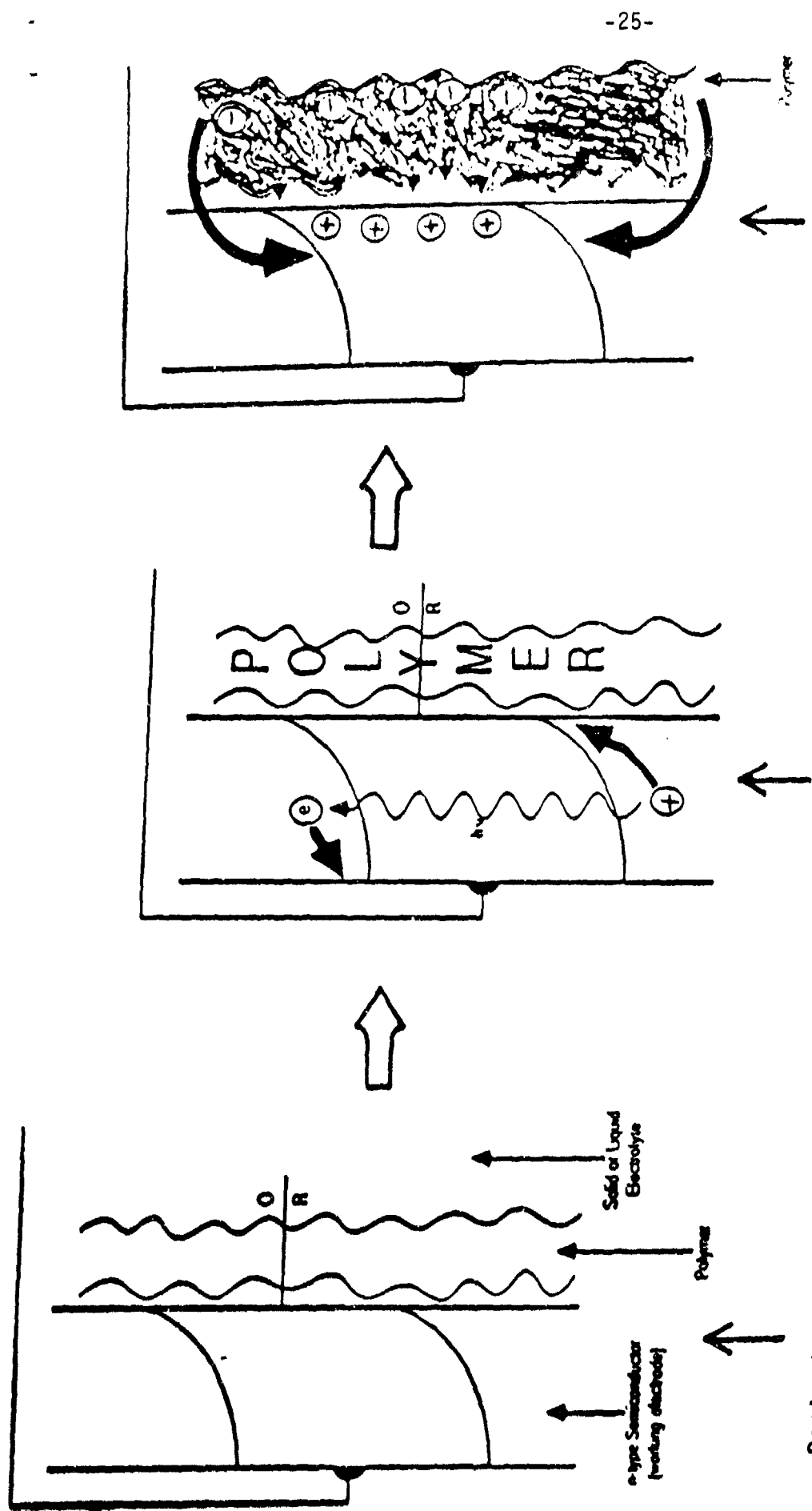


FIG. 1



Rest state

Laser excitation

Charge transport in polymer:
polymer switching

- Processes:
- 1) Photoexcitation of semiconductor (single psec)
 - 2) Charge transfer to polymer (sub-nsec)
 - 3) Oxidation (reduction) of initial polymer layers (ca. 10 - 40 nm) (sub-nsec), thus switching of these layers
 - 4) Charge transport in bulk polymer, switching of bulk polymer (nsec?)

Fig. 2

Fig. 3: Characterization cyclic voltammogram of poly(3-amino pyrazole)/ITO, in Et₄NBF₄/CH₃CN (deoxygenated), 100 mV/sec. (Film thickness ca. 100 nm).

50 uA

0.20 0.10 0.00 -0.10 -0.20
VOLTS vs. Ag/AgCl

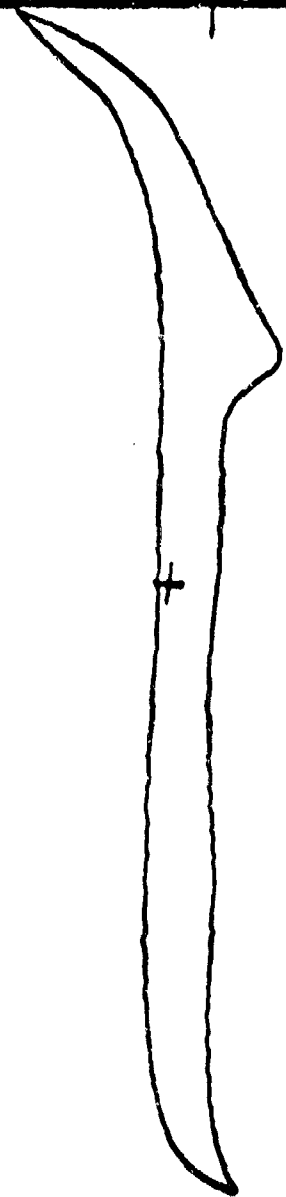


Fig. 4: Characterization cyclic voltammogram for poly(2-amino pyridine)/ITO (ca. 100 nm) in deoxygenated $\text{Et}_4\text{NBF}_4/\text{CH}_3\text{CN}$, 100 mV/sec.

100 μA

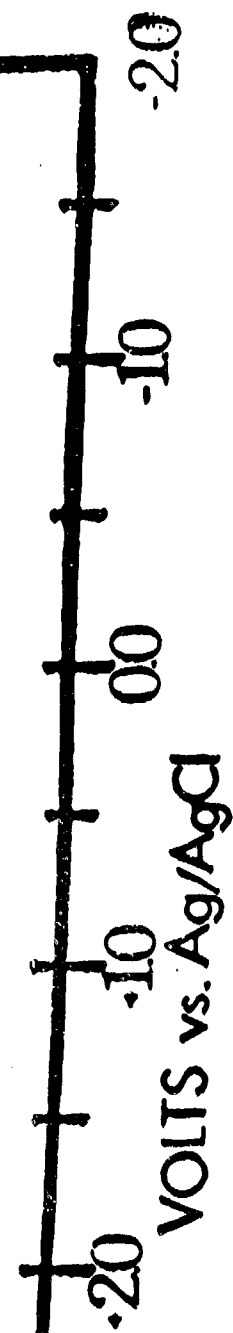
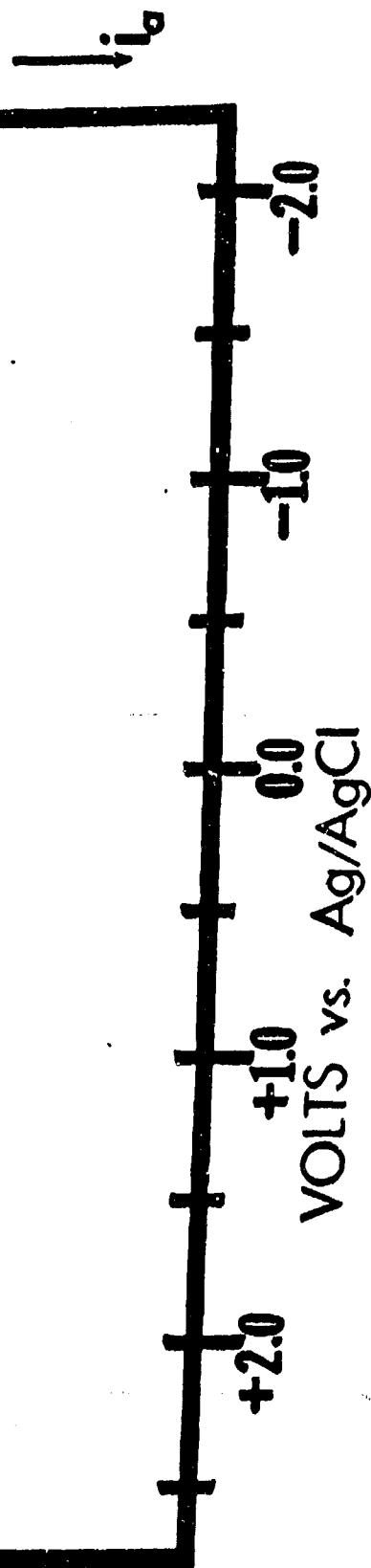
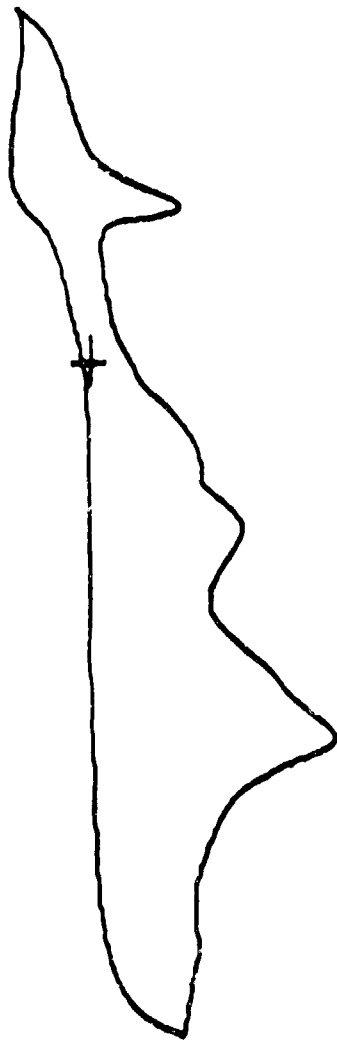


Fig. 5:

Characterization cyclic voltammogram of ca. 100 nm virgin film of poly(1-amino-pyrene) on ITO in deoxygenated Et₄NBF₄/CH₃CN. Scan rate 100 mV/sec.

500 μ A



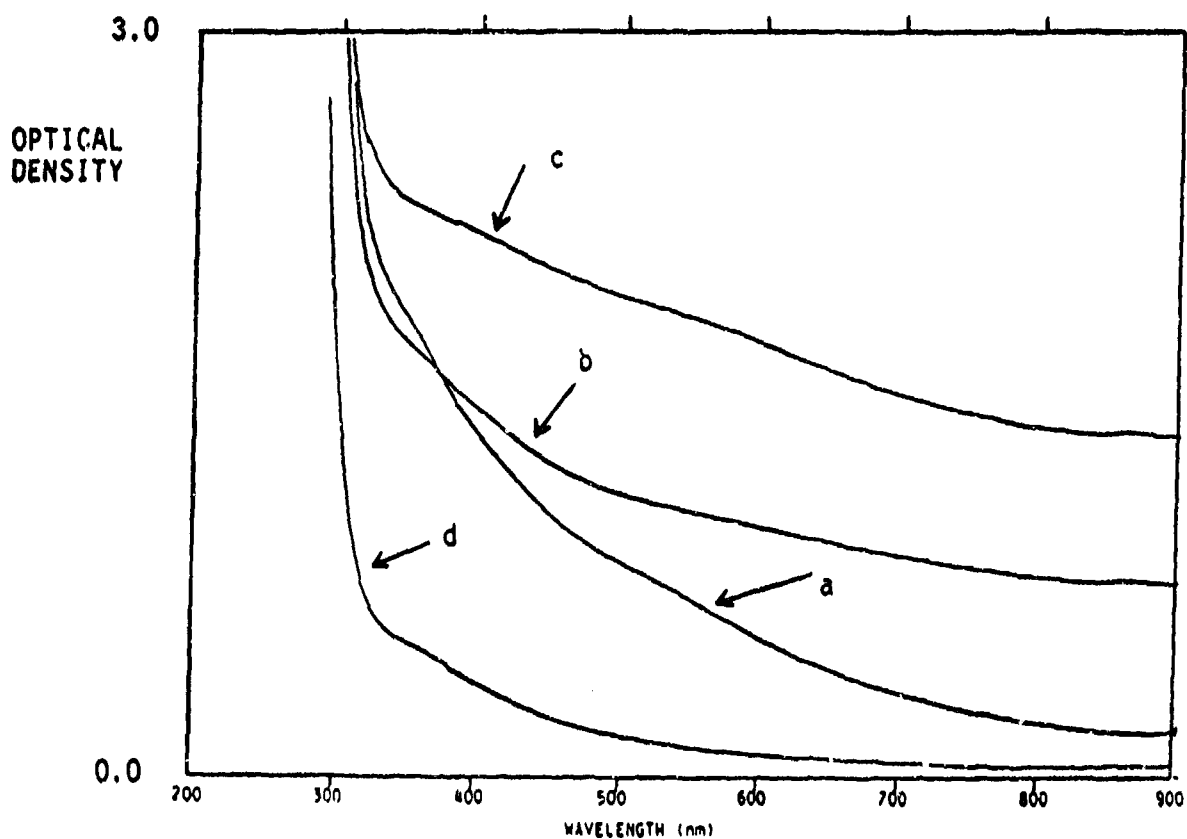


Fig. b: Spectroelectrochemical characterization curve for poly(3-amino quinoline) (P(3AQ)), ca. 75 nm; on ITO, at applied potentials of a) open circuit, ≈0.1 V (fresh film); b) +1.0 V (partly oxidized or doped); c) +2.3 V (highly oxidized or doped); d) -2.0 V (highly reduced or de-doped). All potentials are vs. Ag/AgCl.

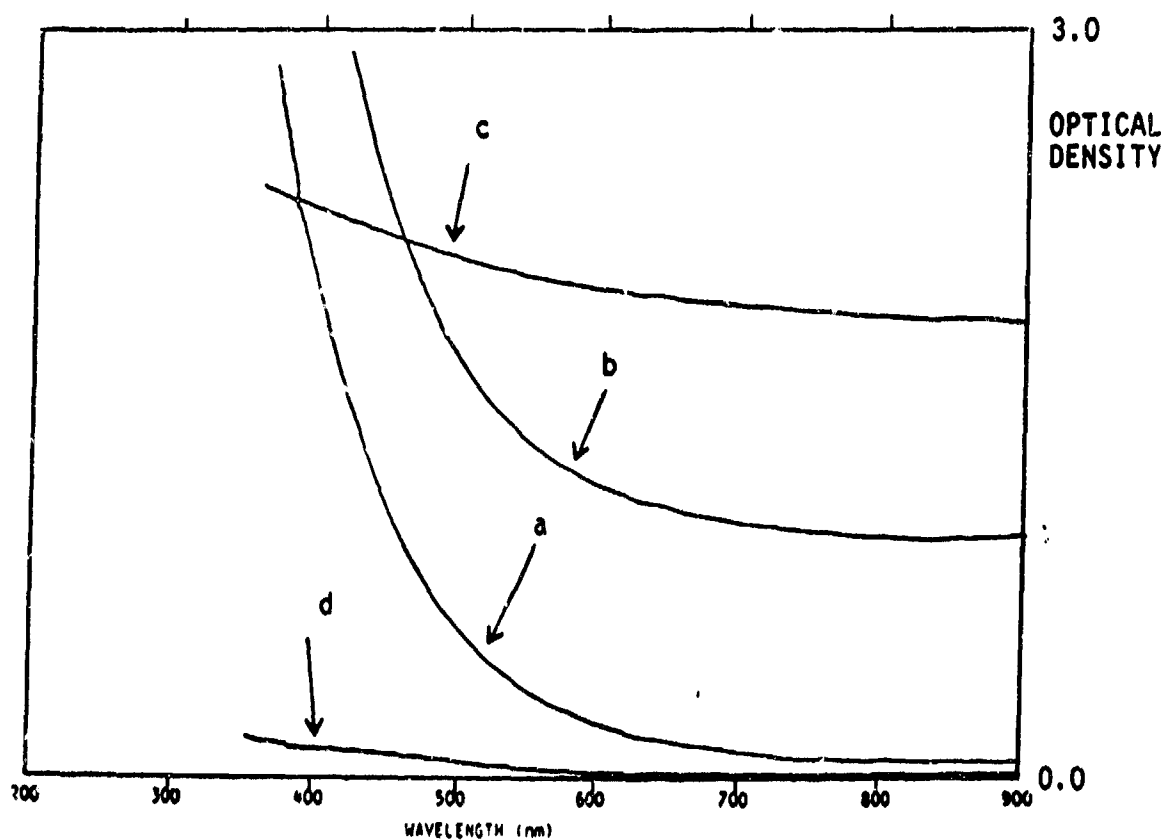


Fig. 7: Spectroelectrochemical characterization curve for poly(2-amino pyridine) (P(2APy), ca. 75 nm, on ITO, at applied potentials (vs. Ag/AgCl) of: a) open circuit, -0.1 V, fresh film; b) +1.0 V, partly oxidized (doped); c) +2.3 V, highly oxidized (doped); d) -2.0 V, highly reduced (de-doped).

3.C

OPTICAL
DENSITY

UV-Vis-NIR spectroelectrochemical characterization curve for poly(1-amino-pyrene), ca. 100 nm, virgin film, on ITO, in deoxygenated Et₄NBF₄/CH₃CN. a) Oxidized form, applied potential +0.8 V; b) as-prepared form (open circuit, +0.17 V); c) reduced form, -0.8 V, all vs. Pt.

Fig. 8

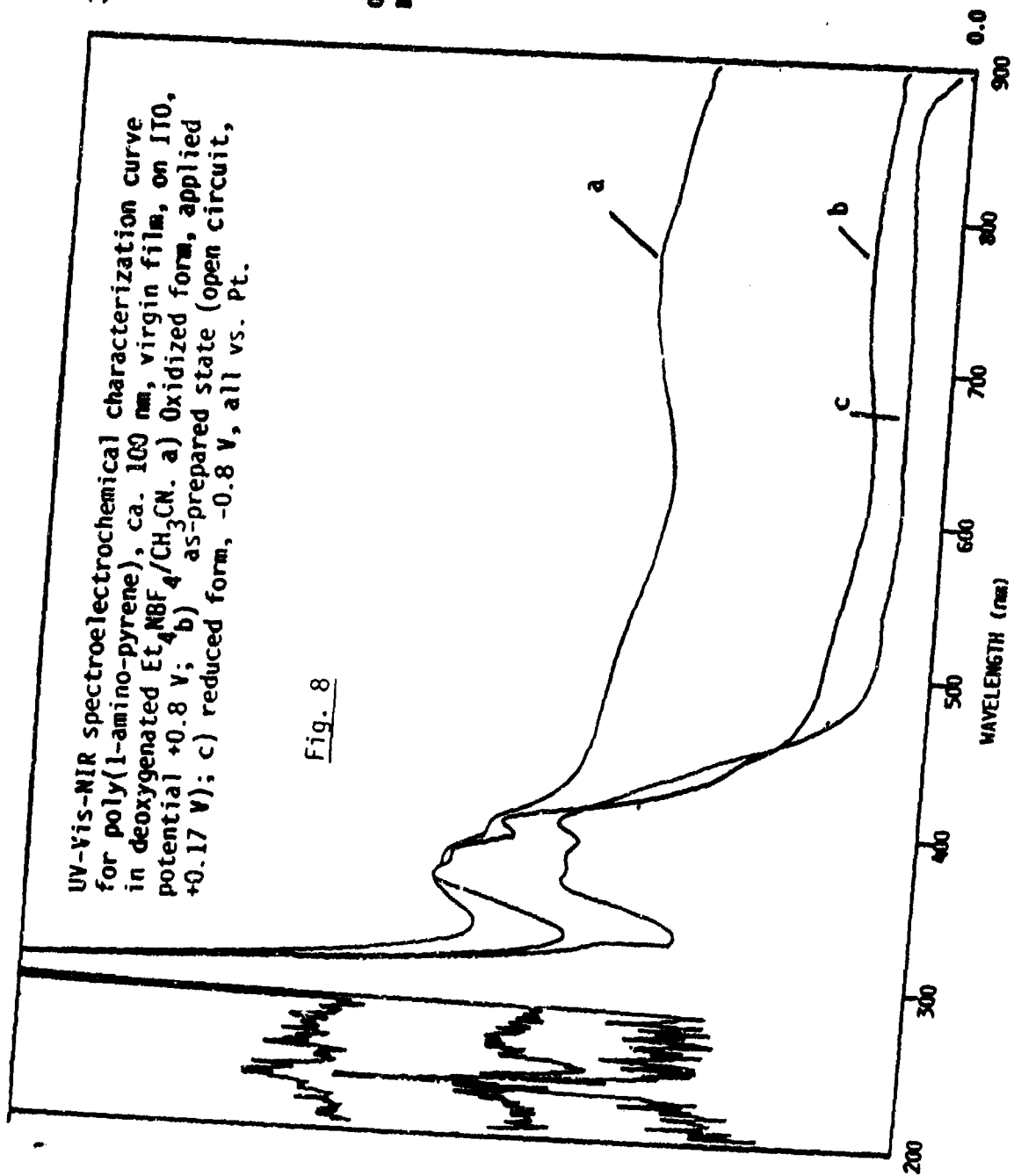


FIG 9:

Transient absorption (TA), pump and probe
at Regional Laser and Biotechnology Laboratories (RLBL),
U. of Pa (Hochstrasser group)

- Pump at 532 or 355 nm (also 1064 nm), ca. 8 ns pulsewidth
- 100 shots at 10 Hz averaged
- Probe 400 - 800 nm, at 0 ns (nominal) to 200 us delays
- yields indication of whether polymer switching is
broad-band or not

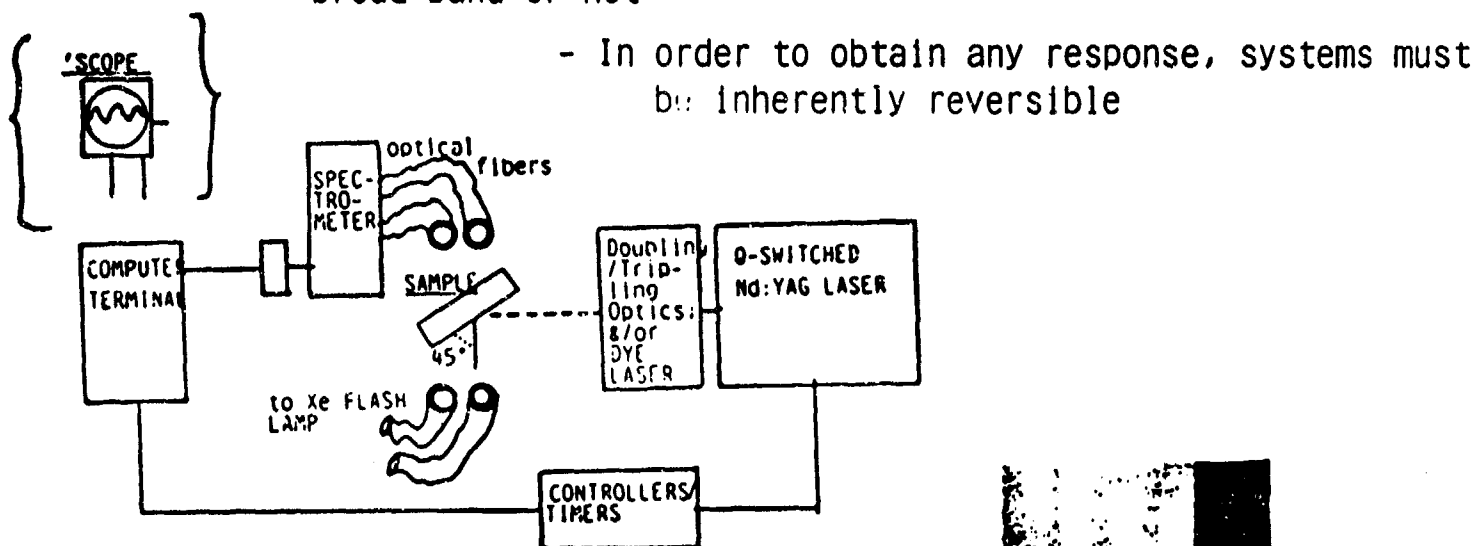
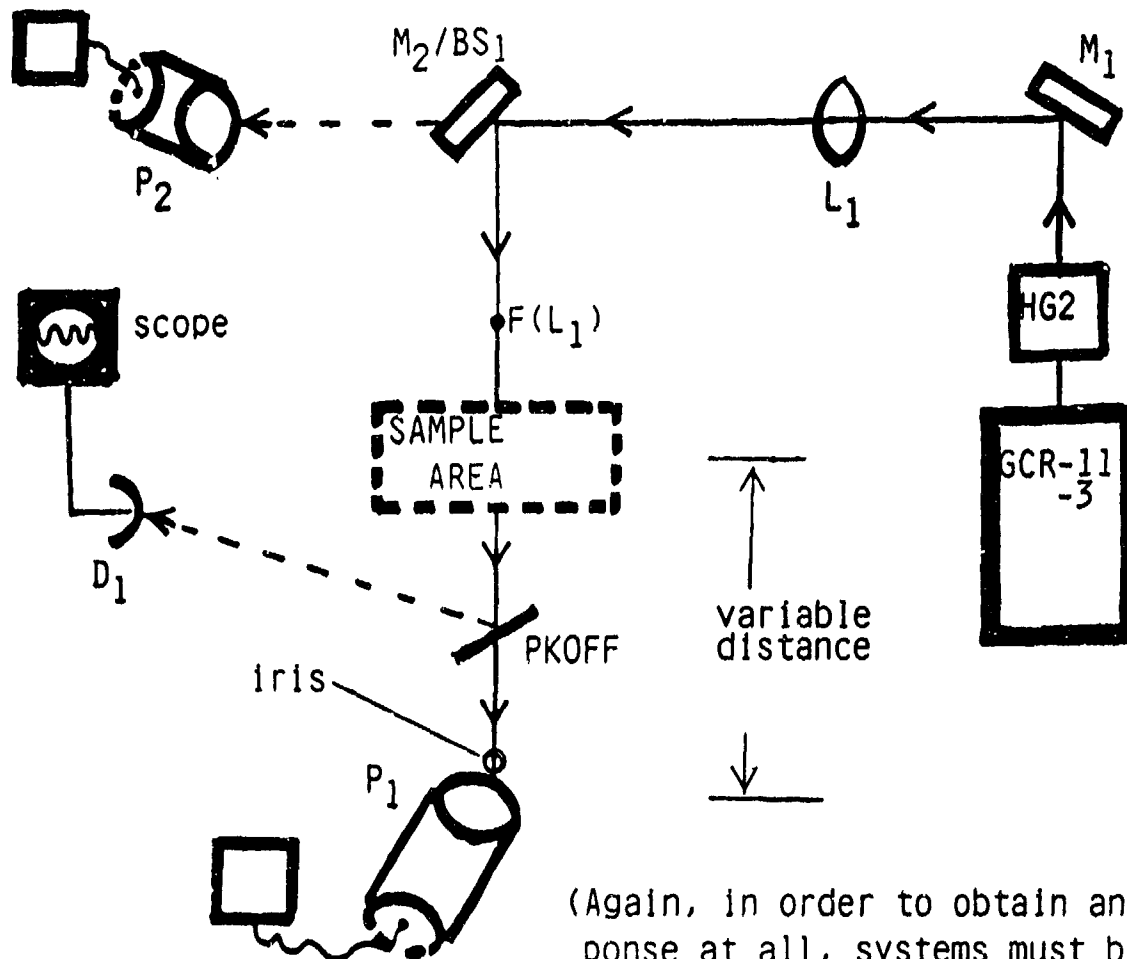


FIG. 10

In-house "direct method" setup



(Again, in order to obtain any response at all, systems must be inherently reversible)

GCR-11-3: Q-switched pulsed Nd:YAG laser (Spectra-Physics)

Pulsewidth adjustable 2.5 - 6 ns

HG2: Frequency doubling and tripling crystals

M₁: 45° high power laser mirror (CVI)

L₁: Focussing lens: 50 cm FL (CVI), w/AR coat (CVI)

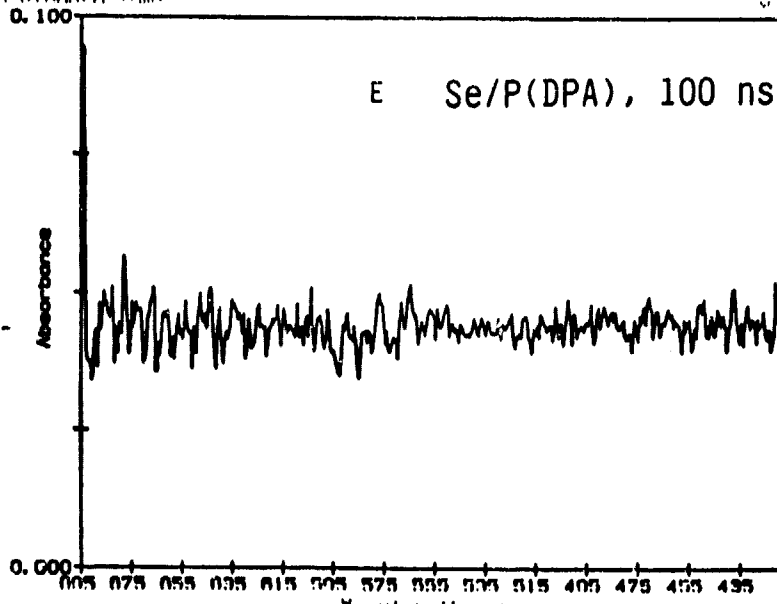
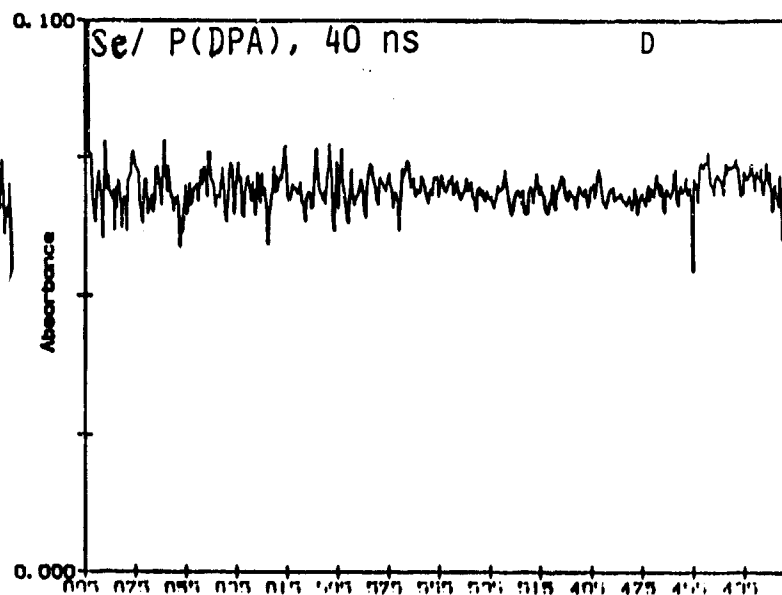
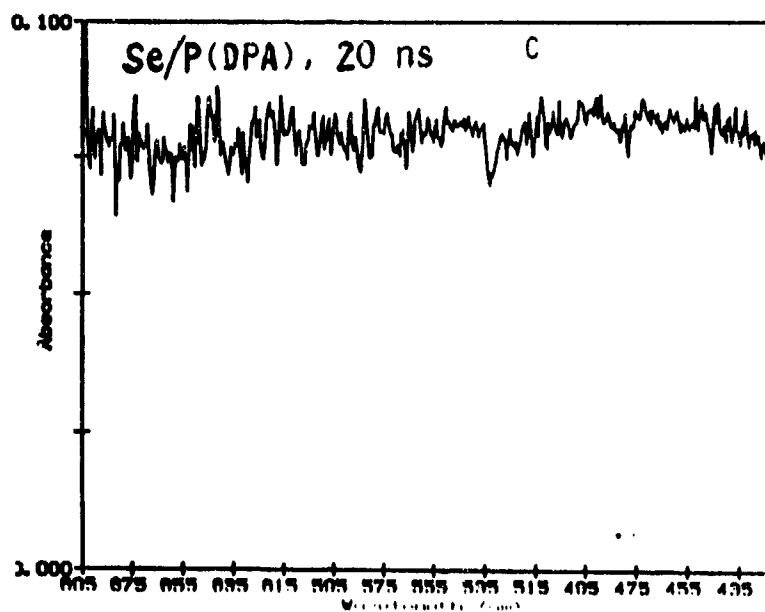
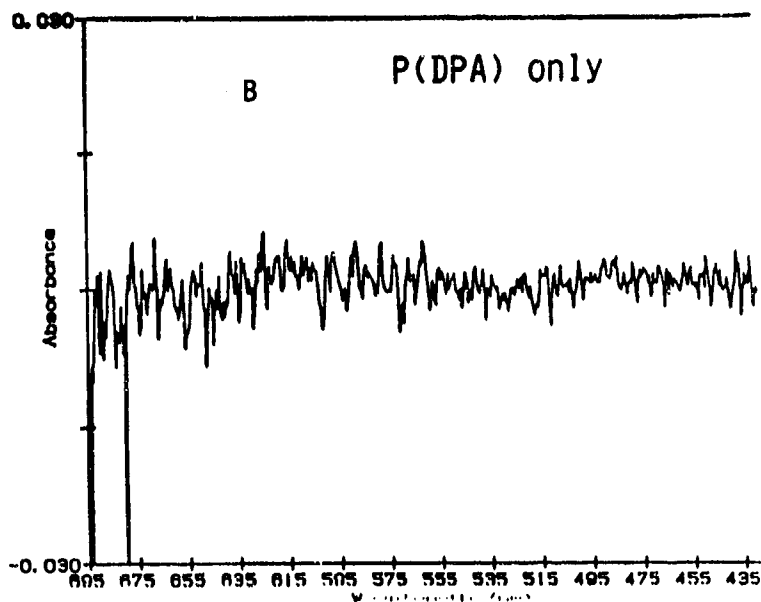
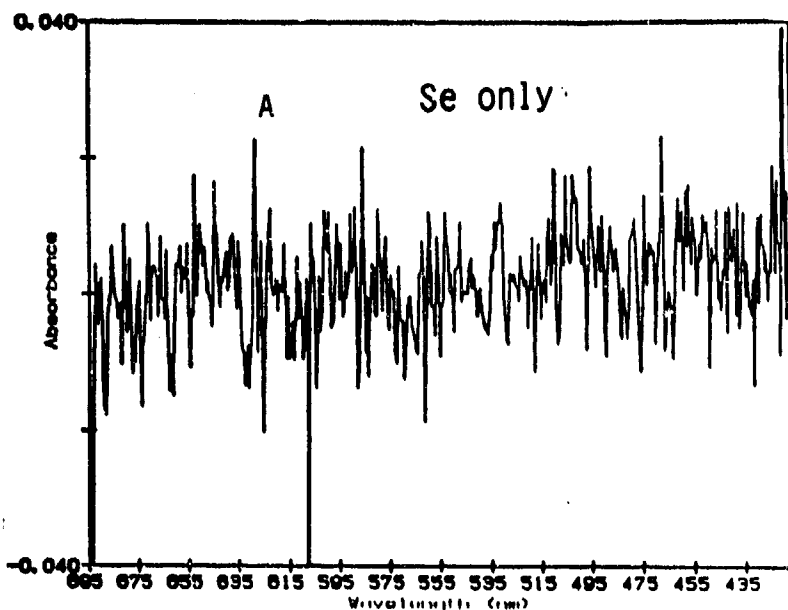
M₂/BS₁: 45° high power laser mirror or beam splitter w/AR coat (CVI)

PKOFF: 1% reflection coated optic (or cover glass) pickoff (CVI)

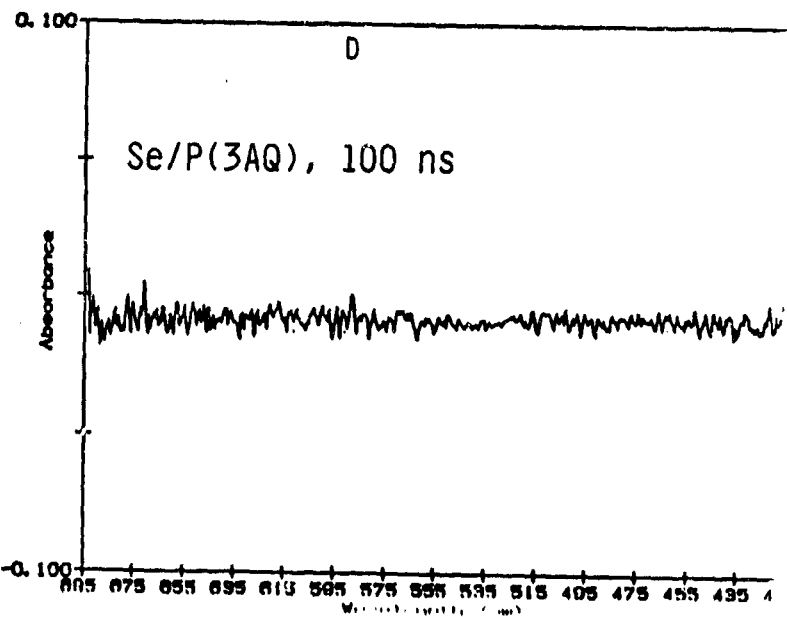
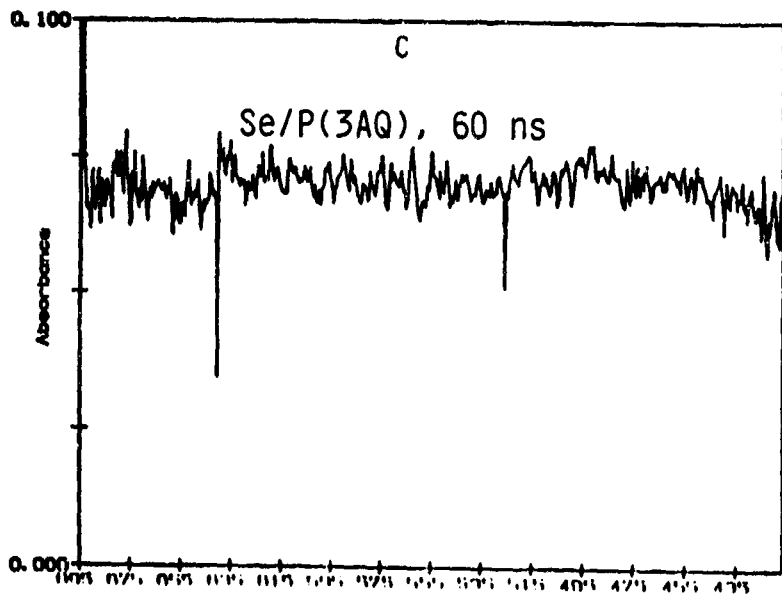
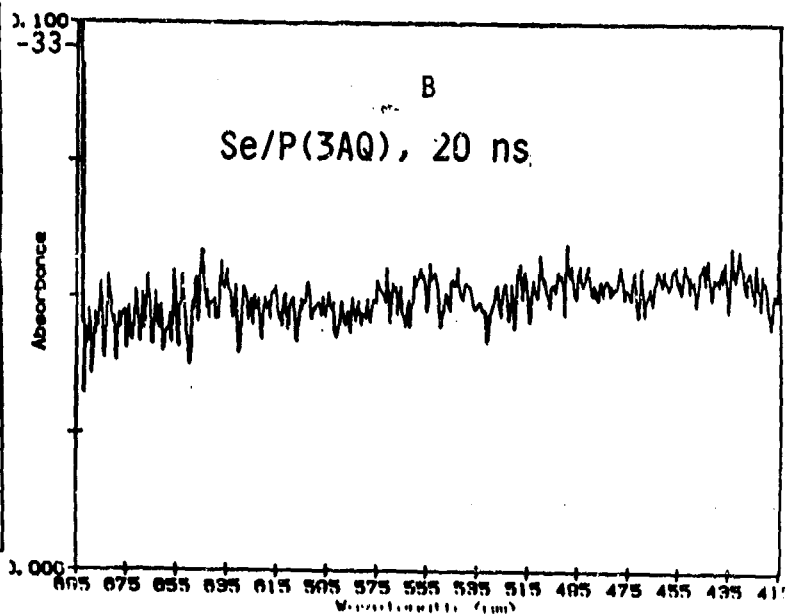
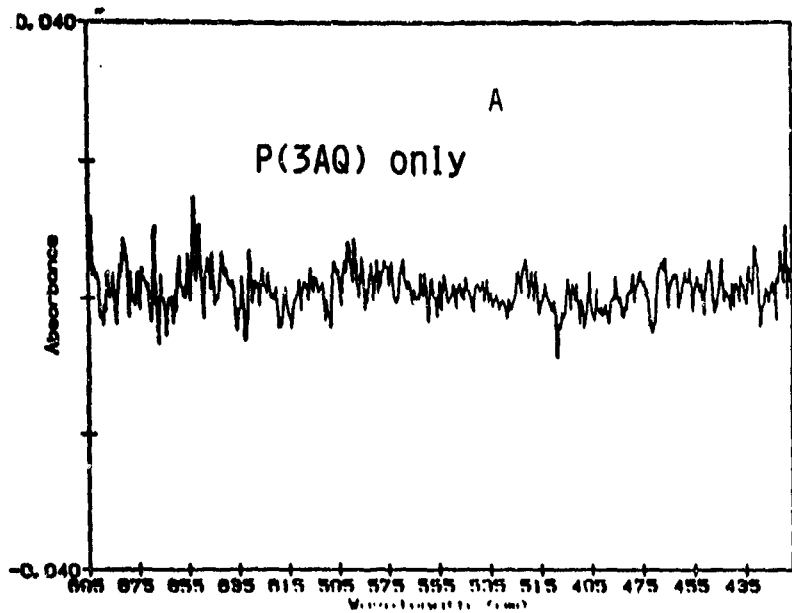
D₁: ultrafast (ca. 400 ps risetime), large-area photodiode (Antel Optronics)

P₁: Power meter w/ digital readout (Scientech)

P₂: Second power meter w/ digital readout for reference measurements (Scientech)

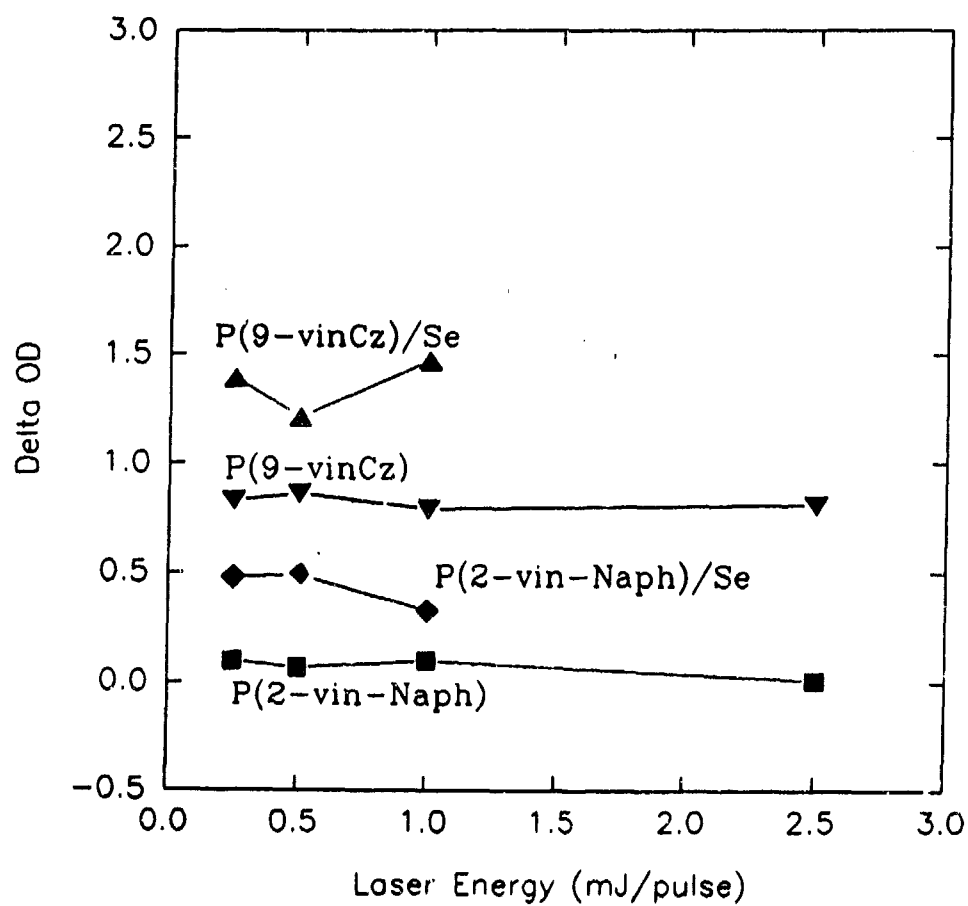


Se/P(DPA)
TA spectra
Figs. 11A-E



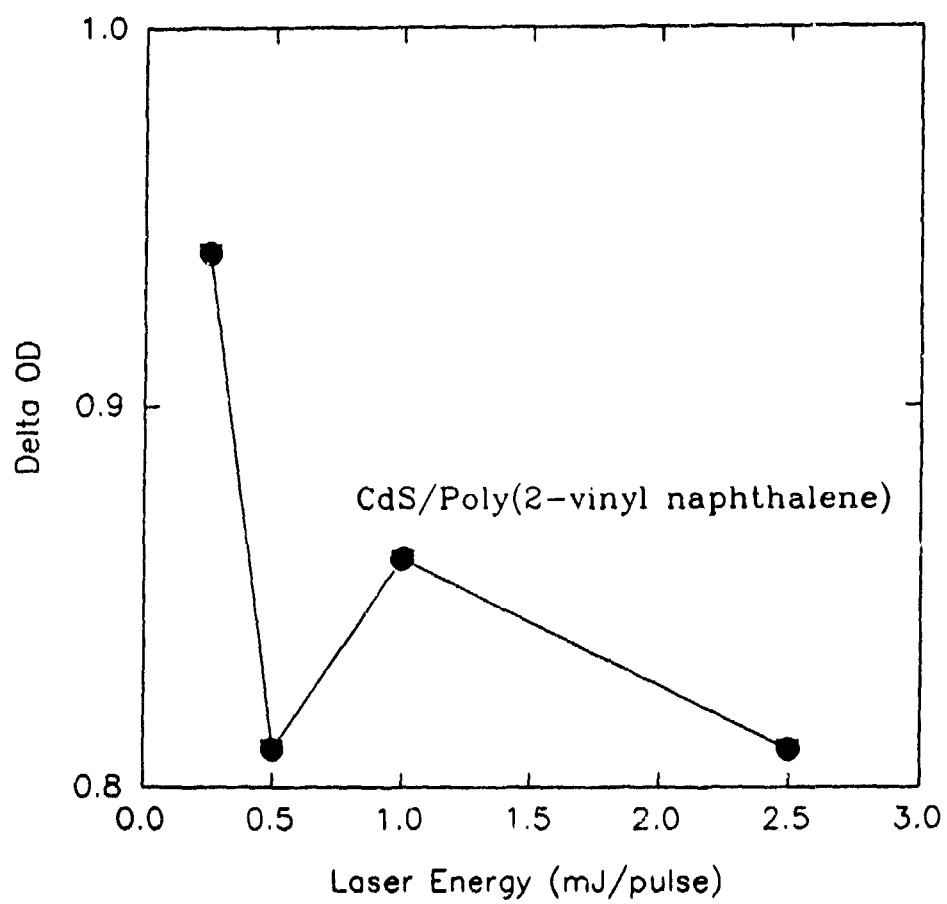
Se/P(3AQ) system, TA spectra
Figs. 12A-D

FIG. 13



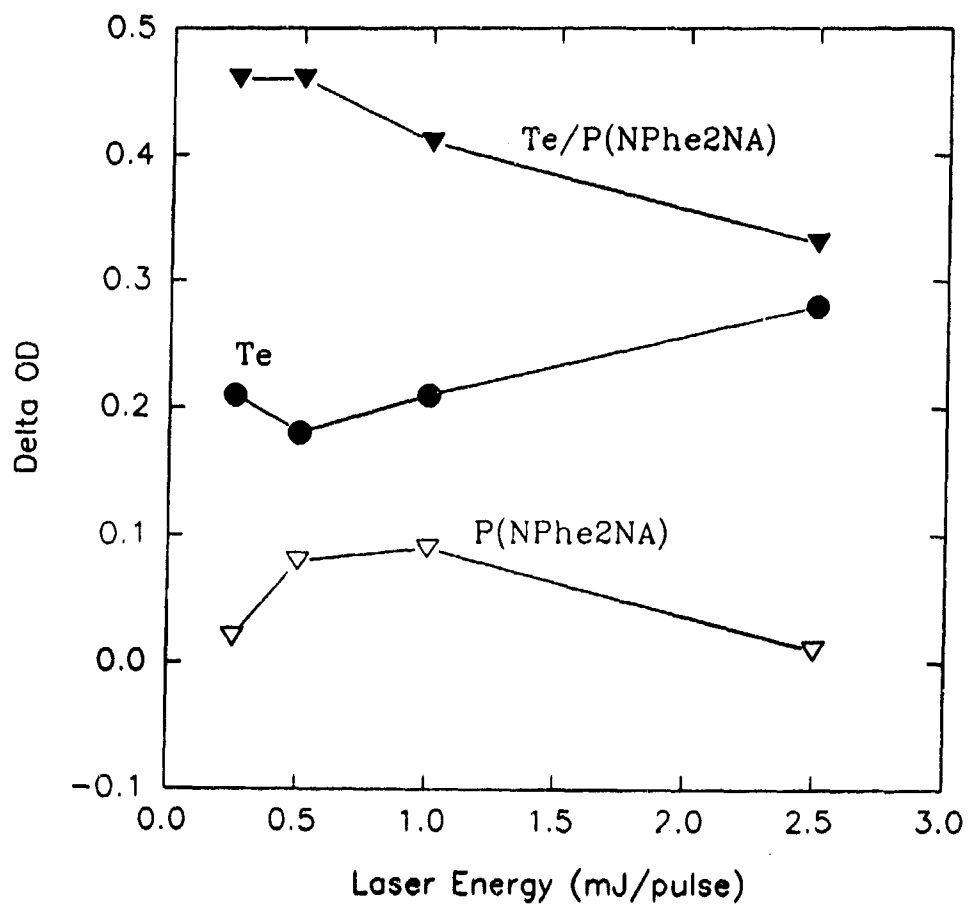
Laser shielding efficiencies. P(9-vinCz)=
poly(9-vinyl carbazole); P(2-vin-Naph)=
poly(2-vinyl naphthalene).

FIG 14



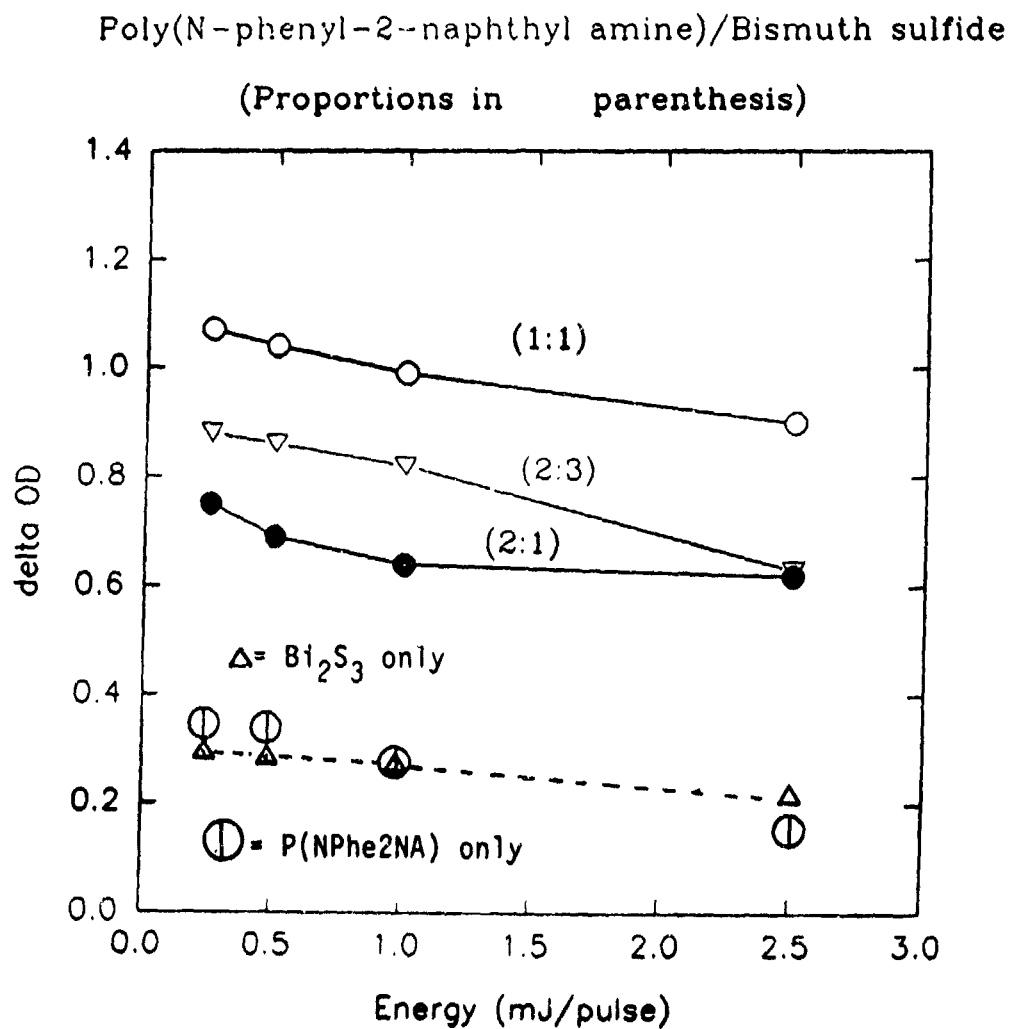
Laser shielding efficiencies.

Fig. 15



Laser shielding efficiencies
P(NPhe2NA)= poly(N-phenyl 2-naphthyl amine)

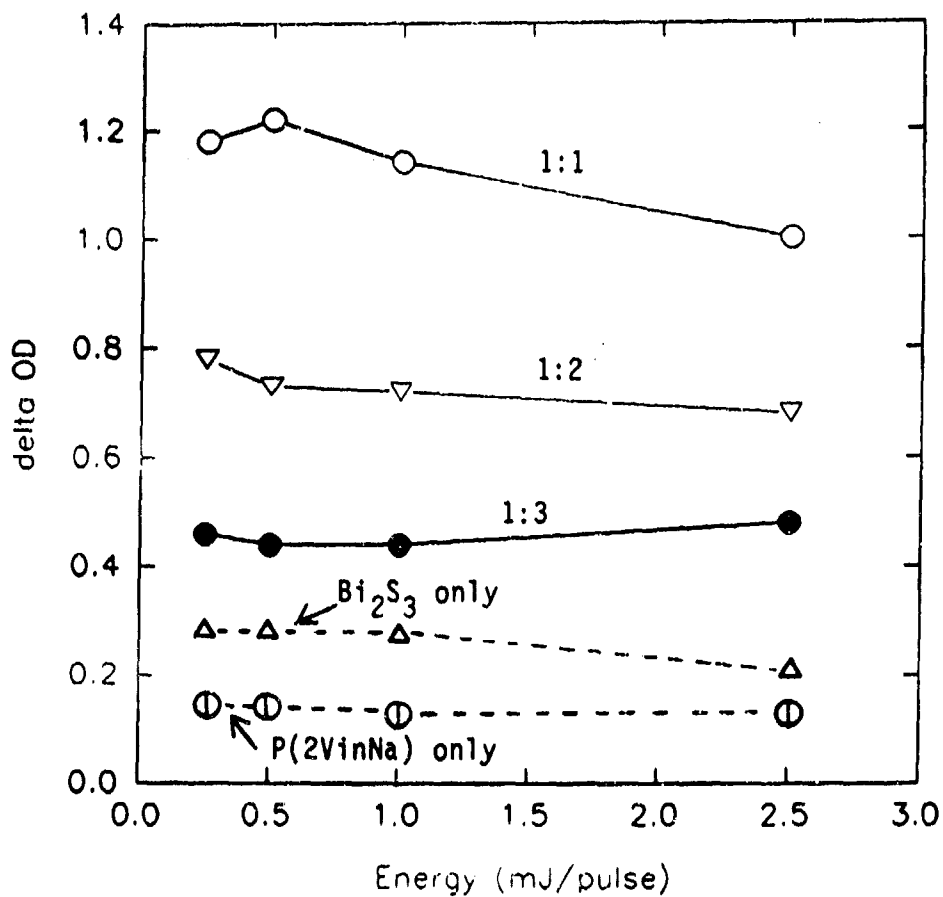
Fig. 16



Laser shielding efficiencies for the P(NPhe2NA)/ Bi_2S_3 combination. The efficiencies for Bi_2S_3 and P(NPhe2NA) alone are also shown, and it is evident that the SC-CP combination has greater shielding than the sum of its parts, clear indication of laser-induced SC to CP charge transfer. Supporting this, the shielding is highest for the SC:CP proportion 1:1.

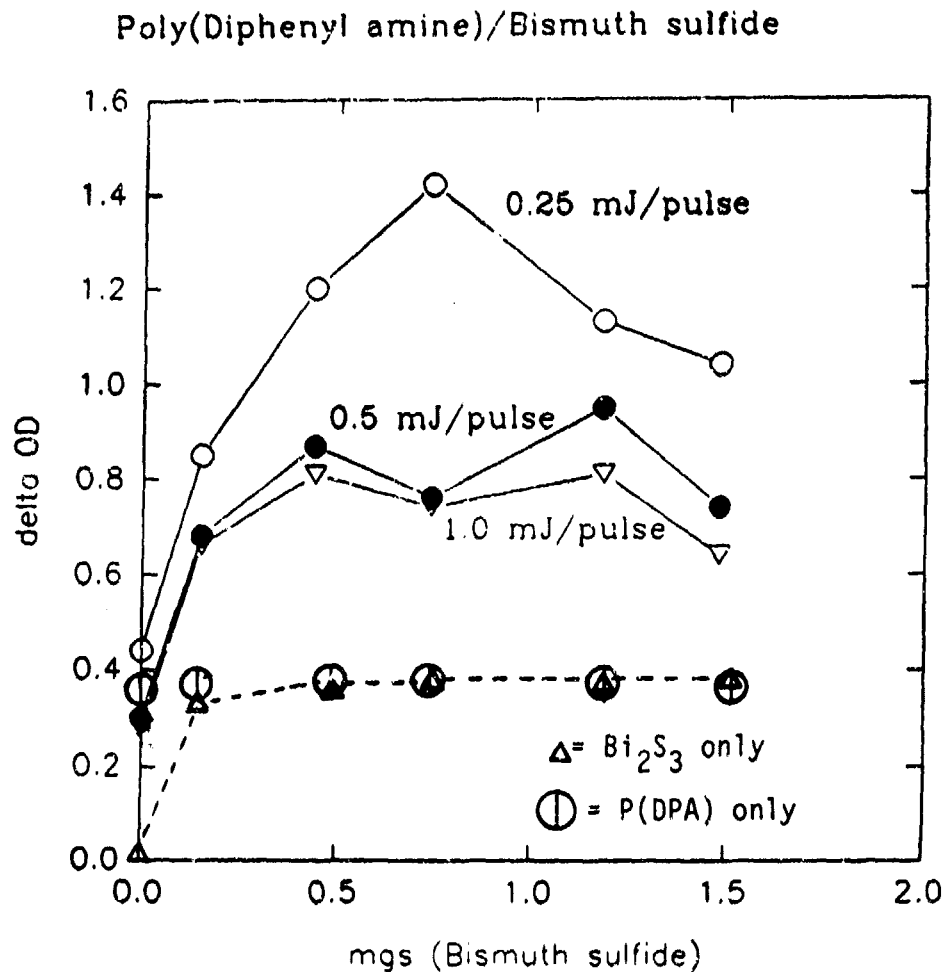
Fig. 17

Poly(2-Vinyl naphthalene)/Bismuth sulfide
(Proportions in parenthesis)



Laser shielding efficiencies for the P(2VinNa)/Bi₂S₃ combination and for equivalent thicknesses of Bi₂S₃ and P(2VinNa) only. Again, clear evidence for SC to CP charge transfer is present, and laser shielding efficiency increases as the SC:CP proportion approaches 1:1.

Fig. 18



(overleaf):

Laser shielding efficiencies for the Bi₂S₃/P(DPA) combination. Again the shielding for the SC/CP combination is higher than the sum of the shielding for SC and CP only. Decrease in shielding at higher incident laser intensities is due to sample thermal ablation, a problem being currently addressed. Variation in proportion of Bi₂S₃ shown, with mgs(P(DPA)) = 1.0.

Fig. 19

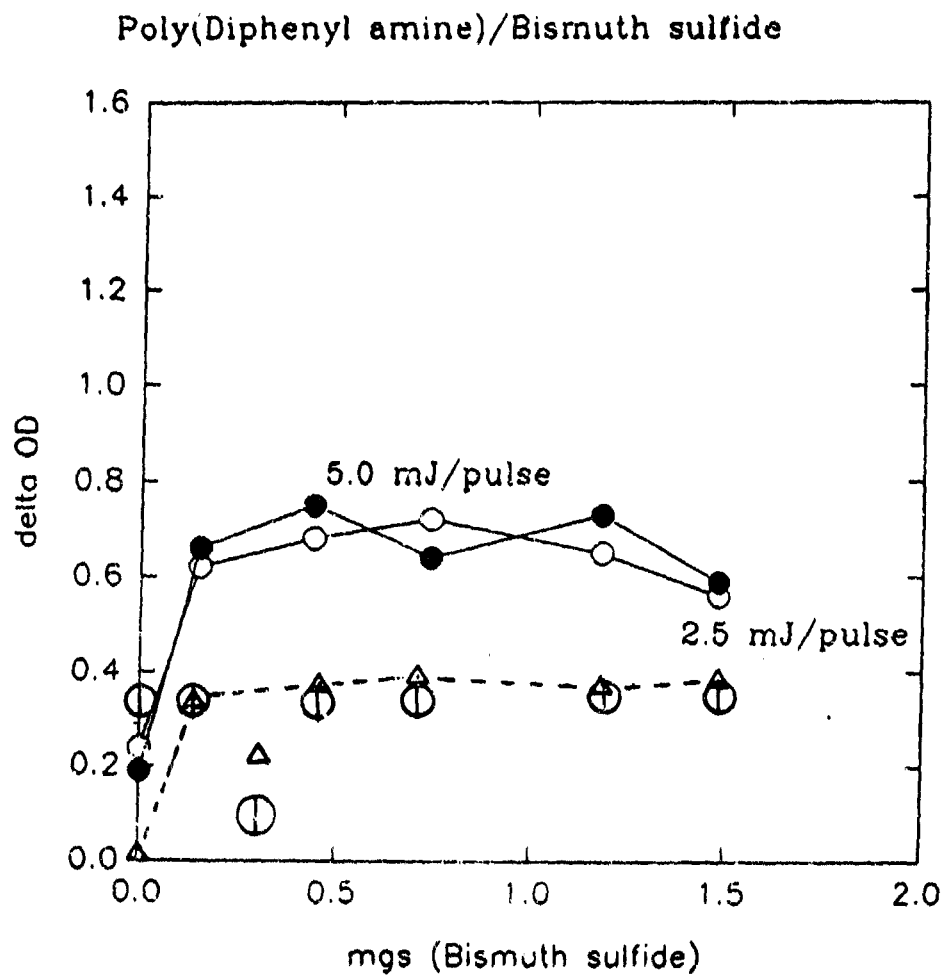


Fig. 20

Poly(Diphenyl amine)/Bismuth sulfide

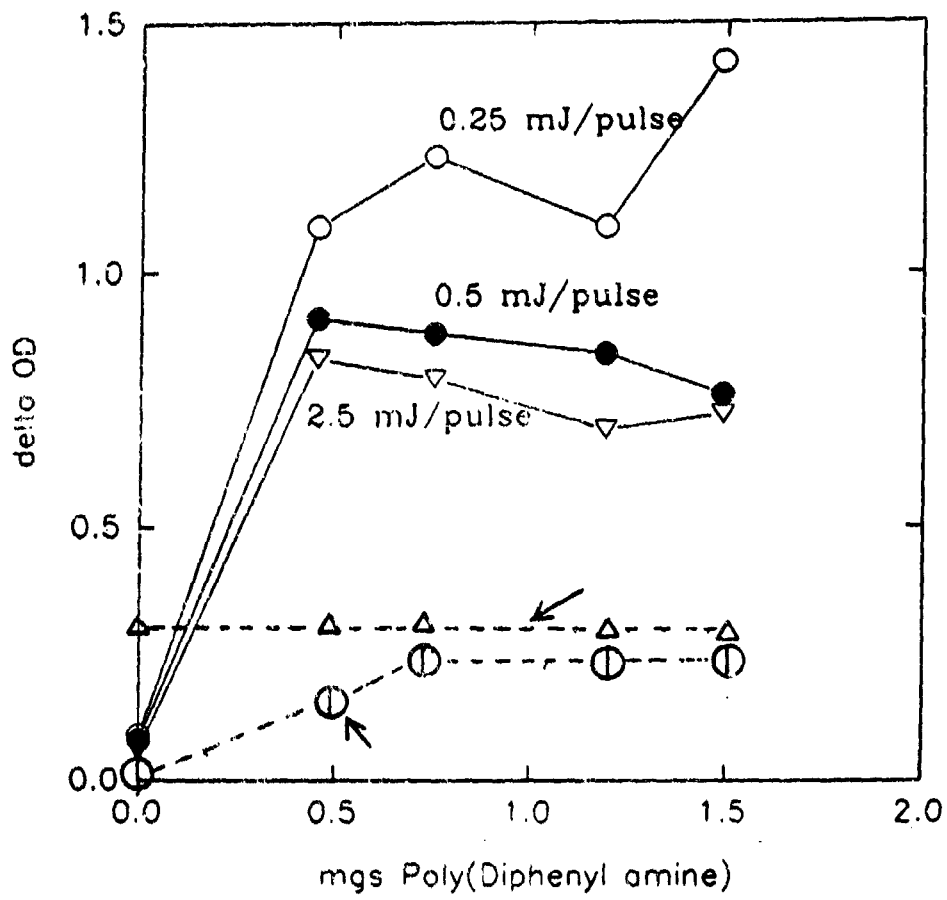
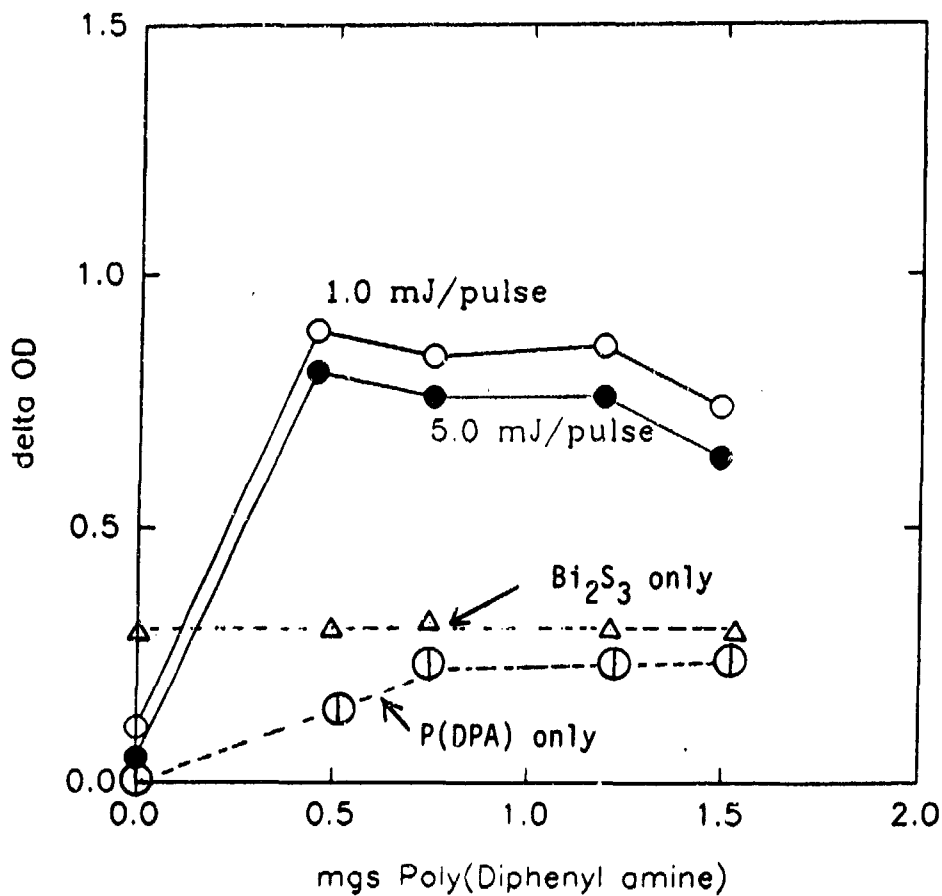


Fig. 21

Poly(Diphenyl amine)/Bismuth sulfide



Laser shielding efficiencies for the Bi₂S₃/P(DPA) combination, with variation in P(DPA) concentration (mgs(Bi₂S₃) = 1.5). Again, cumulative SC-CP shielding is larger than the sum of its SC-only and CP-only parts.