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OPTICAL PROCESSES AND DEVICES USING HYDROGEN BONDED
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Annual Report for Period 1 August 1996-31 July 1997

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Bolling Air Force Base, DC 20332-0001

Executive Summary

This report is presented in three parts: Experiments on Presently Known Materials, New Materials, and Materials for Optical Limiting. Each part is separately referenced and has its own figure numbering and captions.

This year's work has made significant progress on several topics. Our observation that the surfaces of urethane-substituted polydiacetylenes(PDA) that were polymerized by ^{60}Co gamma radiation in the presence of air show conical eruptions on the main crystalline face has been extended to PDA-DCH crystals where an "etching" of the main crystal face is observed by atomic force microscopy. A caveat concerning the need to polymerize these materials in the absence of air has been communicated. α -Cinnamic acid crystals that undergo solid state photodimerization when irradiated with ultraviolet light also show conical eruptions when exposed to uv light when air is present, but not when argon is the atmosphere during irradiation. In our attempts to observe photochromic behavior in urethane-substituted PDA other than PDA-PUDO, irradiation at 532 nm of PDA-ETCD and the ethyl urethane of 5,7-heptadecadiyn-1-ol led to irreversible conversion to the red form. New work toward identifying materials that will be useful in optical limiting has been initiated. The tetrabutylammonium salt of nickel bis-benzene-1,2-diselenolate has been found to be a reverse saturable absorber. In the interest of identifying new hydrogen-bonded PDA other than urethanes that exhibit chromic phenomena, primary amine substituted diacetylene monomers have been synthesized.

Introduction

This annual report will summarize experimental work carried out between 1 August 1996 and 31 July, 1997. It will generally have a similar organization to our proposal University of Massachusetts Lowell Research Foundation #95-009. The Abstract of UMLRF 95-009 is given below as a guide to the experimental approach. Additionally, we have initiated work toward the design, synthesis, and characterization of new conjugated materials for optical limiting applications, and this work is presented below.

Abstract of UMLRF 95-009

The objective of the work described herein is the detailed chemical and physical characterization of hydrogen-bonded polydiacetylenes (PDA) of interest for optical device applications, including optical memory, optical storage, holographic elements, and spatial light modulators. The features of the known PDA with urethanes as the hydrogen-bonded group that make them attractive materials for optical device fabrication relate to a first order chromic phase transition and are summarized. Using physico-chemical sound rationale, new materials involving replacement of some of the hydrogen bonding groups with esters or carbonates are designed and proposed for study. The new materials are expected to exhibit the chromic phase transition under defined experimental conditions such that ultimate optical device performance will be enhanced. In addition to urethanes, diacetylene monomers containing amides and ureas as hydrogen bonding groups will be synthesized and polymerized. The resulting polymers will be studied in both single crystal and thin film form, as well as self-assembled morphologies. An important scientific result that should emerge from this research is a complete crystallographic characterization of a PDA at temperatures below and above the chromic phase transition. The information that will be available from these structural studies will allow a quantitative assessment of possible mechanical strains in the structures of these materials. Refractive index changes due to photochromic effects will be accurately measured by recording a holographic grating. The exploration of quadratic electrooptic effects for photorefraction, observed in quantum wells and inorganic semiconductors, will be attempted in these materials.

Experiments on Presently Known Materials

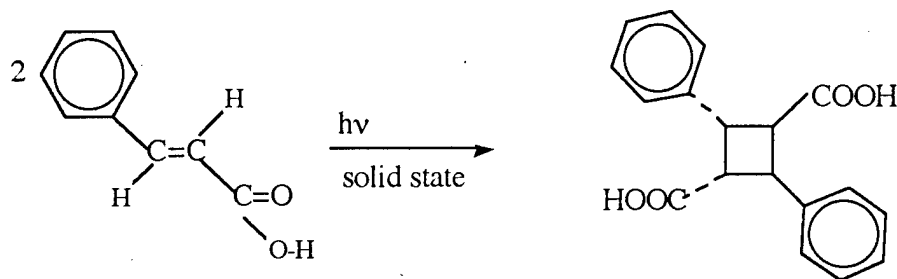
1. Atomic Force Microscopy (AFM).

Atomic Force Microscopy Studies of Crystals That Undergo Solid State Reaction Initiated by Ultraviolet or Ionizing Radiation

AFM¹ has become a major tool in the study of the surface morphology of organic molecular and polymeric materials²⁻⁴, both as single crystals and thin films of materials that are electrical insulators. AFM is particularly well suited for the study of crystals undergoing solid state reaction⁵ initiated by ultraviolet(UV) light or ionizing radiation, such as ⁶⁰Co γ radiation, because reaction will initiate near the crystal surface.

We have recently reported⁶ that AFM studies of single crystals of diacetylene(DA) monomers that are dialkylurethanes of 5,7-dodecadiyn-1,12-diol reveal anisotropic surface eruptions on the [100] faces of these crystals when they are irradiated with ⁶⁰Co γ radiation in the presence of air, but not in its absence. The eruptions on the average are 0.5 microns at the base and about 700 Å in height. They appear after about 1 Mrad of radiation at a dose rate of 1 Mrad/hr. in a process requiring about 50 Mrad for complete conversion to polymers that are thermochromic and reported⁷ to be photochromic for the case of the bis-n propylurethane(PUDO). Crystals having surface eruptions are irreversibly converted from their blue form to a red form at room temperature on exposure to a single pulse of 532nm light while crystals lacking the eruptions do not undergo this change. Hence the interaction of laser light with these crystals is critically dependent on the details of the surface morphology of the crystals.

In view of the role of air in the surface eruption process, we wondered if other materials undergoing solid state reaction would exhibit related behavior. In view of our continuing interest^{8,9} in mechanistic and spectroscopic aspects of the solid state dimerization of cinnamic acids, we chose to investigate α -cinnamic acid. The solid state dimerization of α -cinnamic acid to truxillic acid is illustrated in Scheme 1.



Scheme 1. Solid state dimerization of α -cinnamic acid to truxillic acid.

EXPERIMENTAL SECTION

Cinnamic acid was obtained from Aldrich Chemical Company and recrystallized from benzene or ethanol. The crystals were identified as a phase¹⁰ from their X-ray powder pattern with the aid of the program "Micro D-space", Materials Data, Inc., Livermore, California. AFM imaging was carried out using a Park Scientific Instruments Autoprobe cp scanning probe microscope under ambient conditions. The images were obtained in the noncontact mode using silicon cantilevers (2mm ultralevvers, Park Scientific, force constant = 25 N/m) at a resonant frequency of about 200 kHz. The tip radius was specified to be about 250Å by Park Scientific as seen from high resolution scanning electron micrographs. An 80 mm scanner was used. The AFM images did not change when irradiated samples were examined at a time more than 24 hours after initial imaging. Irradiation at 370 nm was carried out using four 15 watt Sylvania 2051 sources as previously described.⁹ The peak output of these lamps is 370 nm but they emit a broad range of wavelengths. For AFM study, single crystals were placed on mounts so as to expose the largest face and these were irradiated along with loose crystals. Irradiations were carried out in a cell with a quartz window either in the presence of air or under static argon. Circulating water controlled the temperature of the cell to 20°C, and the lamp-to-sample distance was 8 cm. After irradiation, the degree of dimerization of the bulk sample was determined by proton nmr spectroscopy using a Bruker instrument at 250 MHz in acetone- d₆ solution. The amount of conversion of cinnamic acid to truxillic acid dimer in the sample was estimated from the relative areas of the vinylic protons of cinnamic acid at δ 6.5-6.6 and the aliphatic protons of the truxillic acid dimer at δ 3.8 and 4.4.

RESULTS AND DISCUSSION

Samples of cinnamic acid were irradiated at 370 nm for 48 hours in the presence of air. Study of the bulk irradiated samples by proton NMR revealed that the cinnamic acid in the samples was 5.0-7.6%

converted to truxillic acid. AFM examination of the main face of irradiated crystals revealed eruptions that were 0.2 microns in diameter at the base and approximately 200 angstroms in height. These eruptions are somewhat smaller than those found on the polymerizing DA monomers⁶ discussed above. The AFM image of a pristine cinnamic acid crystal is displayed in Figure 1, and the image of a crystal irradiated in air is shown in Figure 2. The appearance of these eruptions is qualitatively similar to those previously observed⁶ in diacetylene polymerizations. Eruptions are also observed on cinnamic acid crystals irradiated in air using 254 nm light. These observations of a substantially changed crystal surface are in general accord with a previous report concerning UV irradiation of *cinnamic acid* in the presence of air.¹¹

Somewhat different observations were made when cinnamic acid crystals were irradiated at 370 nm under a static argon atmosphere. Figure 3 shows the AFM image of a crystal taken from a batch where the bulk conversion was 10.6% irradiated under argon for 48 hours. Note that while the surface is significantly rougher than the pristine surface shown in Figure 1,

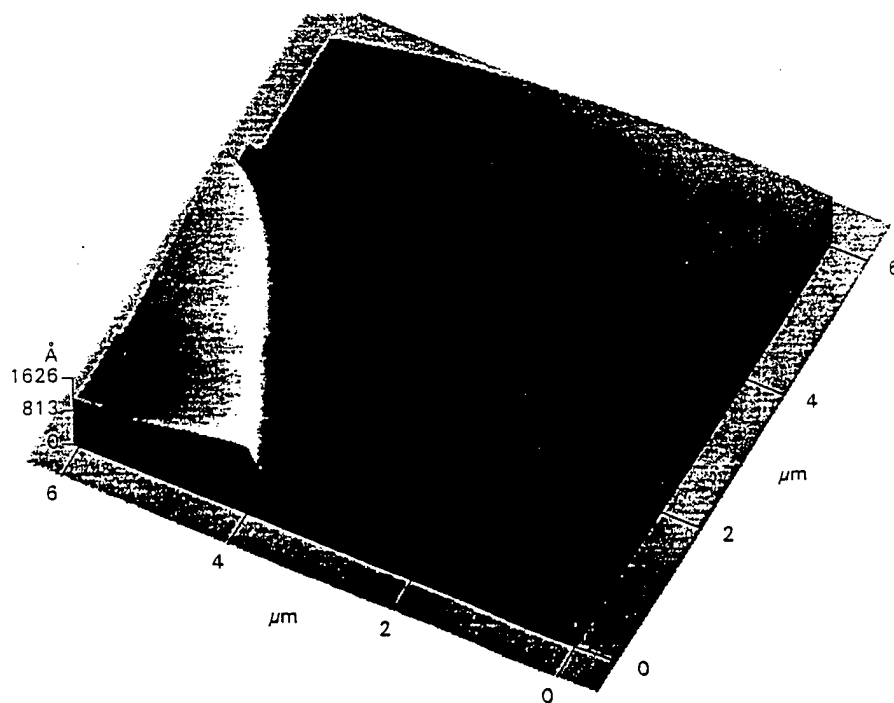


Figure 1. AFM image of the main face of a pristine cinnamic acid crystal.

this image lacks the features of the erupted surface shown in Figure 2. Hence, under the conditions described herein, the surface morphologies of α -cinnamic acid crystals are different depending on whether or not air was present during irradiation. An earlier study¹¹ reported that the same features were observed on the [010] face of α -cinnamic acid independent of whether UV irradiation was carried out in air or under vacuum.

Examination of crystals of α -cinnamic acid irradiated under argon by optical microscopy on the AFM stage and elsewhere revealed a range of behavior. While some crystals revealed virtually no change upon irradiation, others revealed extensive cracking along the long dimension of the crystal.

In summary, we have observed that, like DA crystals of the dialkylurethanes of 5,7-dodecadiyn-1,12-diol, crystals of α -cinnamic acid show different surface morphologies depending on whether or not the crystals are irradiated in the presence of air.

AFM STUDIES OF REACTIVE CRYSTALS

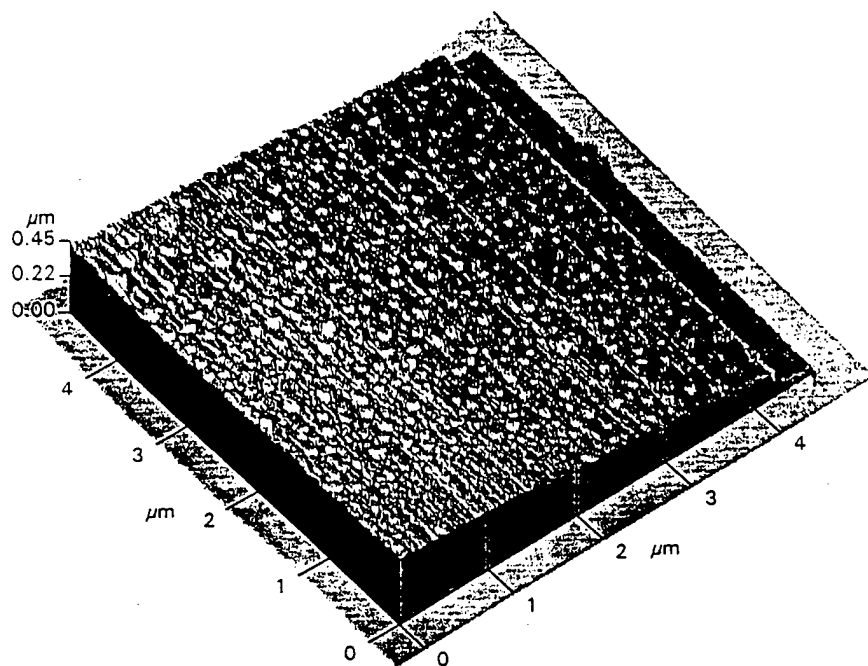


Figure 2. AFM image of the main face of a crystal of cinnamic acid irradiated at 370 nm in the presence of air. Note the conical eruptions covering the surface.

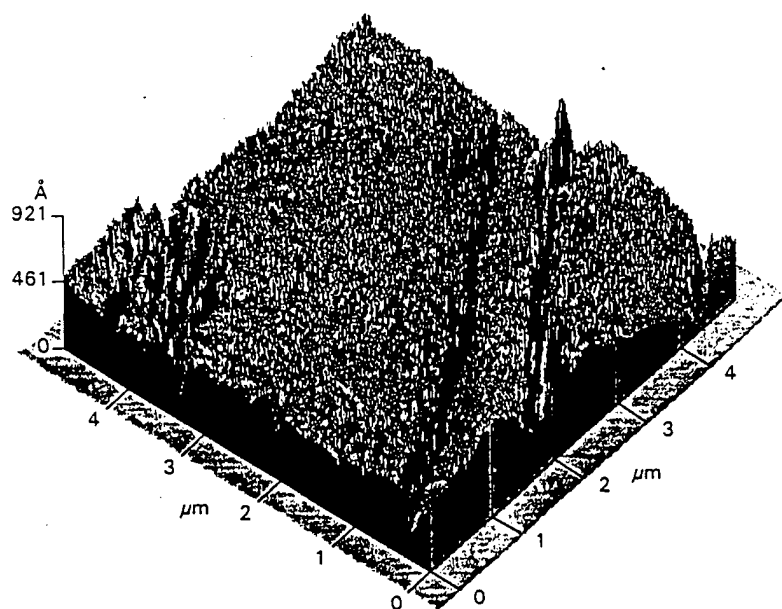


Figure 3. AFM image of the main face of a crystal of cinnamic acid irradiated at 370 nm under argon. Note the development of cracks.

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Some Comments on Experimental Aspects of the Use of Ionizing Radiation to Initiate Solid State Reactions

Ionizing radiation has been a major tool for the initiation of solid state reactions, especially polymerization, at least since the 1951 report of the interaction of an electron beam with ethyleneglycol dimethacrylate.¹ The penetrating character of the ionizing radiation to all matter allows processes to occur that do not occur, for example, with uv radiation. While uv light can initiate solid state polymerization of diacetylene(DA) monomers, the stronger absorption of the initially formed polymer prevents complete monomer-to-polymer conversion unless the thickness of the experimental sample allows penetration of the light. To obtain completely polymerized bulk single crystals of the melt-stable dialkylurethanes of 5,7-dodecadiyn-1,12-diol(1a-c), it is necessary to use ionizing radiation.² To obtain bulk single crystals of the polydiacetylene (PDA, 1) of 1,6-di-N-carbazolyl-2,4-hexadiyne(DCH), it is necessary to use ionizing radiation, as the thermal process converts single crystal monomer to polycrystalline polymer.³

In the use of ionizing radiation for synthetic purposes, it is important to keep in mind the range of reactions that can be initiated by radiation. The interaction of ionizing radiation with the atmospheric gases nitrogen and oxygen leads to the formation of ozone and the oxides of nitrogen.⁴ Hence, it is important to know if an irradiation was performed on a sample in the presence of air or on an evacuated sample. For the specific case of DA monomers, it is appropriate to recall that ozone and oxides of nitrogen can initiate polymerization

PDA-DCH ; polymerized in the presence of air;
60 Mrads; 1 Mrad/hr

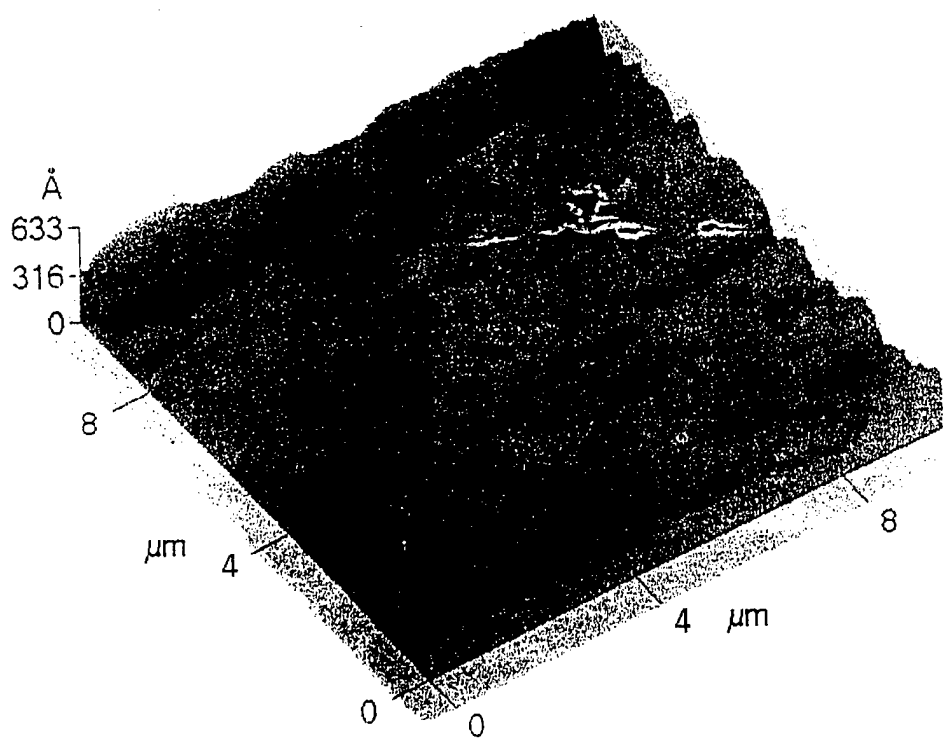


Figure 4.

in the absence of radiation.⁵ Additionally, solids prepared by crystallization from solution can include solvent in crystalline defects, and this included solvent can initiate reactions that would otherwise not occur,⁶⁻⁸ especially when the solvent contains heavy atoms such as chlorine.

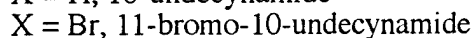
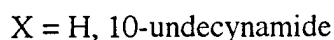
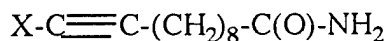
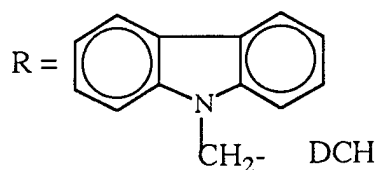
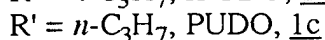
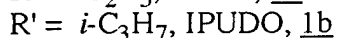
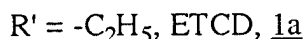
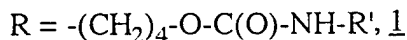
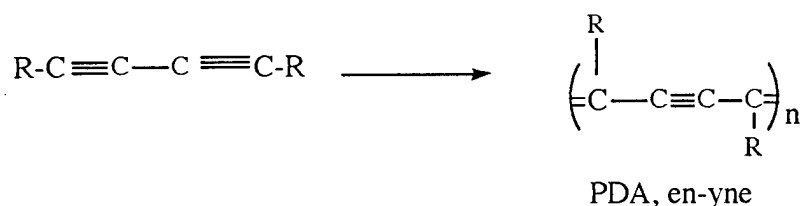
Nevertheless, in spite of the reactivity of ionizing radiation toward virtually anything, many publications that report the use of radiation in synthetic experiments do not detail the specific experimental conditions under which an irradiation was performed. Specifically, one does not know what total dose was used, what dose rate was used, or what was the nature of the atmosphere above the sample undergoing irradiation. A parameter such as dose rate is important because the rate of product formation in radiation-induced chain processes depends on it.⁹

The preparation of this report was motivated by three different experiments carried out in our laboratories in recent years that revealed an important difference in the product of an irradiation depending on whether the process was carried out in the presence or absence of air. This is especially critical for crystals of interest for their linear and nonlinear optical properties, such as PDA. In such crystals, light interacts first with the crystal surface. Hence the quality of the surface is of paramount interest for such crystals. We summarize this experimentation here in the hope that other experimenters will detail specific experimental conditions involved when ionizing radiation is used for bulk synthetic experiments. Scheme 1 shows the experimental systems under discussion and an illustration of the diacetylene polymerization.

RESULTS AND DISCUSSION

We have recently reported¹⁰ that Atomic Force Microscopy (AFM) studies of single crystals of diacetylene (DA) monomers that are dialkylurethanes of 5,7-dodecadiyn-1,12-diol reveal anisotropic surface eruptions on the [100] faces of these crystals when they are irradiated with ⁶⁰Co γ -radiation or electron beams in the presence of air, but not in its absence. The eruptions on the average are 0.5 microns at the base and about 700 Å in height. They appear after about 1 Mrad of radiation in a process requiring about 50 Mrad for complete conversion to polymers that are thermochromic and reported¹¹ to be photochromic. Crystals having surface eruptions are irreversibly converted from their blue form to a red form at room temperature on exposure to a single pulse of 532 nm light while crystals lacking the eruptions do not undergo this change. Hence, the interaction of these crystals with laser light is critically

dependent on the surface morphology of the crystals, and that, in turn, depends on the specific details of the irradiation process.



Scheme 1. Molecular structures under discussion and illustration of the diacetylene polymerization.

In additional recent work¹², we have found that the surface morphology of PDA-DCH crystals, as revealed by micron-scale AFM study, depends on whether or not the polymerization is carried out in the presence of air. For polymerization carried out in the absence of air, the [100] face of PDA-DCH crystals¹³ reveals a generally smooth fibrous morphology. In the presence of air, the [100] surface of the crystals is markedly less fibrous and reveals regions where significant etching has occurred. A typical etched surface region is displayed in Figure 4, along with the surface of a crystal polymerized in the absence of air. Such etching was not observed in our studies of the alkylurethanes already reported.¹⁰ Ozone and oxides of nitrogen would be less reactive toward the aliphatic groups and urethane groups that are near the [100] surface of the thermochromic PDA crystals¹⁰ than they would be toward the carbazole groups exposed by the morphology of PDA-DCH crystals.¹³

A third system studied recently is 11-bromo-10-undecynamide.¹⁴ Our interest in this compound followed from our earlier crystallographic and spectroscopic studies of the solid state reactivity of monoacetylenes, particularly 10-undecynamide.¹⁵ In spite of crystallographic C-C contacts between potentially reactive

acetylenic carbons as short as 3.66 and 3.75 angstroms¹⁵, 10-undecynamide is unreactive on exposure to 50 Mrad doses of ⁶⁰Co γ -radiation in either the absence or presence of air. For 10-undecynamide, excitation at all wavelengths between 120-300 nm leads to light emission at wavelengths greater than 300 nm.¹⁵

In the interest of enhancing the reactivity of a crystalline monoacetylene via a heavy atom effect, we synthesized 11-bromo-10-undecynamide.¹⁴ 11-Bromo-10-undecynamide is reactive toward both 254 nm uv light and ⁶⁰Co γ -radiation. In the latter case, the product is an amorphous polyacetylene. When 11-bromo-10-undecynamide is irradiated with 50 Mrad ⁶⁰Co γ -radiation in the absence of air at ambient temperature, the product obtained is a dry solid, m.p. 66-71°C, while a similar irradiation in the presence of air leads an oily solid, m.p. 55-71°C. Both solids have a similar conversion to polymer.¹⁴ The crystal structure of 11-bromo-10-undecynamide¹⁶ reveals that the interaction between acetylene groups is different than that of 10-undecynamide.

CONCLUSIONS

Above, we have discussed three monomeric systems that undergo solid state polymerization under the influence of ionizing radiation, especially ⁶⁰Co γ -radiation. The properties of the products are clearly dependent on whether the irradiation was performed in the presence or absence of air. This is particularly important for crystals of interest for their linear and nonlinear optical properties such as PDA. Accordingly, we recommend to investigators who use ionizing radiation for synthetic purposes that they specify as much experimental detail as is meaningful to someone who might attempt to repeat their experiments. Considerations such as temperature, total radiation dosage, radiation dose rate, and the nature of the atmosphere above the sample are clearly very important.

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Figure Captions

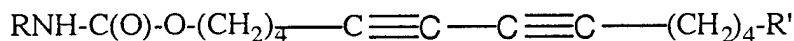
Figure 1: AFM image of the main face of a pristine cinnamic acid crystal.

Figure 2: AFM image of the main face of a crystal of cinnamic acid irradiated at 370 nm in the presence of air. Note the conical eruptions covering the surface.

Figure 3: AFM image of the main face of a crystal of cinnamic acid irradiated at 370 nm under argon. Note the development of cracks..

Figure 4: AFM image of the main face of a PDA-DCH crystal that was polymerized in the presence of air. Note the etching of the surface.

Scheme 1: Diacetylene structures:



- 1a R = C₂H₅; R' = -O-C(O)-NH-C₂H₅ (ETCD)
1b R = (CH₃)₂CH; R' = -O-C(O)-NH-CH(CH₃)₂ (IPUDO)
1c R = C₃H₇; R' = -O-C(O)-NH-C₃H₇ (n-PUDO)
1d R = C₂H₅; R' = (CH₂)₄CH₃
1e R = C₂H₅; R' = -O-C(O)-O-C₂H₅

PDA-DCH Crystals for Nonlinear Optical Study

In the interest of detailed characterization of the third order nonlinear optical properties of PDA-DCH, we have collaborated with Professor George Stegeman, CREOL, University of Central Florida. A sample of DCH monomer was synthesized. Monomer single crystals with excellent optical quality were polymerized by a 50 Mrad dose of ⁶⁰Co gamma radiation and furnished to Professor Stegeman. Optical characterization of these crystals is in progress.

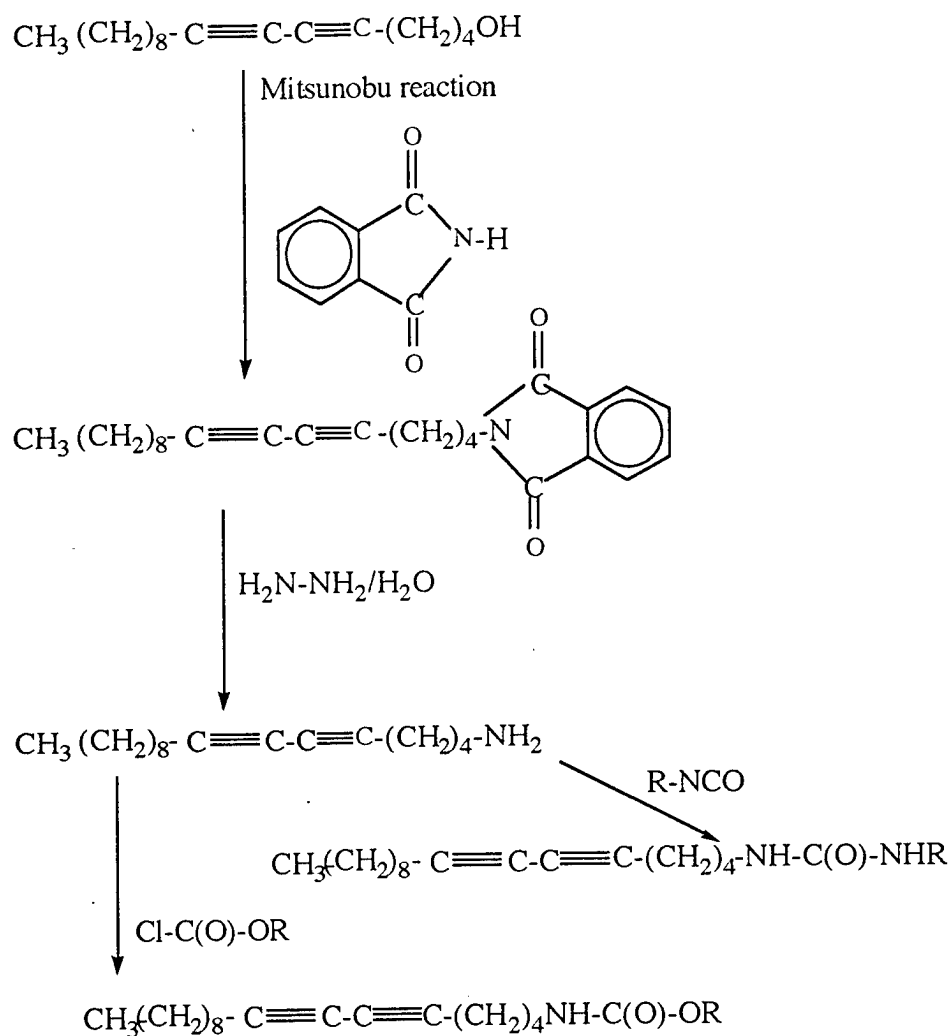
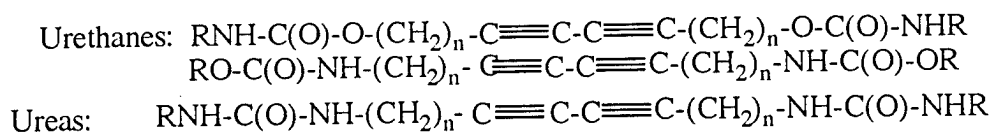
Photochromism in PDA-PUDO

In last year's report, we described the sensitivity of the surface of crystals of PDA-PUDO to the atmosphere above them during radiation induced polymerization. We have obtained a new batch of PDA-PUDO crystals that were polymerized under vacuum, and these will be used to study possible photochromism in this material. We have

also assembled an optical parametric oscillator system, and this should provide both wavelengths and photon densities that will allow detailed assessment of photochromism in PDA-PUDO.

New Materials

In the interest of preparing new hydrogen-bonded PDA with hydrogen bonding groups other than the known urethanes, the synthetic chemistry outlined in the scheme below was undertaken. We expect to have new urethanes isomeric to the known class and ureas in the near future. This should allow a detailed comparison of the role of hydrogen bonding group on spectra and chromic phase transition temperatures.



Proposed synthetic routes to monomers of new chromic hydrogen bonded PDA.

Experimental: All solvents and materials were used as received unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium under inert atmosphere. ^1H NMR spectra were recorded on either Bruker 200 MHz or 250 MHz spectrometers (^{13}C NMR on 50 MHz and 62.9 MHz spectrometers, respectively). IR spectra were obtained on a Perkin Elmer 1760x spectrometer. Melting points

were determined on a Electrothermal Digital Melting Point Apparatus and are uncorrected. Elemental Analyses were performed by either Schwarzkopf Microanalytical (Woodside, NY) or Roberson Microlit Laboratories, Inc. (Madison, NJ).

General Procedure for the preparation of ω -bromo alkyn-1-ols:

Water (105 mL) was placed in the reaction vessel and nitrogen bubbled through for 15 minutes. Sodium hydroxide (1.3 mol) was then added portionwise and the reaction vessel placed in an ice bath. Bromine (0.29 mol) was then added dropwise over 60 min and the reaction mixture then stirred for an additional 15 min under nitrogen. To the vigorously stirred mixture was then added a solution of the alkyn-ol (0.16 mol) in dioxane (90 mL) dropwise over 60 min. After 1 hr. the reaction mixture was diluted with water (300 mL) and extracted with ether (5 x 70 mL). The organic layer was dried over MgSO_4 (anh.), filtered and the solvent removed under reduced pressure to give the crude product, generally pure by ^1H NMR. The products can be further purified by vacuum distillation.

6-Bromo-5-hexyn-1-ol(Lit.¹)(NB-19, JCS-39-3): 72% yield after distillation. bp 70-74°C/0.1 mm; IR (neat) 3348 (OH), 2219 (acetylene) cm^{-1} . ^1H NMR (CDCl_3) δ 1.58-1.66 (m, 4H), 2.20-2.34 (t, $J = 6.5$ Hz, 2H), 2.40 (s, 1H), 3.60-3.71 (t, $J = 6.28$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 19.65, 31.42, 38.57, 62.36, 80.09.

Preparation of heptadeca-5,7-diyne-1-ol (NB155):

In a round bottom flask equipped with gas inlet, magnetic stirred and septa under argon was added 1-undecyne (20 mL, 101.7 mmol), ethanol (56 mL), and hydroxylamine hydrochloride (0.42g, 6.1 mmol). Argon was bubbled through the solution for 30 min. Undecyne was then added followed by ethylamine (20 mL, 234 mmol, 70% in water) to give a bright yellow solution with a yellow precipitate. The yellow mixture was cooled in an ice bath. A deaerated solution of 6-bromo-5-hexyne-1-ol (15 g, 85 mmol) in ethanol (56 mL) was added to the yellow reaction mixture via a syringe pump (8.8 mL/hr) over 7 hrs. (Solid hydroxylamine hydrochloride was added occasionally (3 x 0.5 g) to remove the blue

¹ W. Kim, thesis, U. Mass. Lowell, 1994 p38.

color of Cu^{2+} .) The reaction mixture was allowed to warm to room temperature and stirred overnight. The lime-green reaction mixture was extracted with ether (6x20 mL) and the combined extracts washed with water (3 x 60 mL) and then dried over anhydrous MgSO_4 , filtered and then evaporated. The crude product was chromatographed (550 g SiO_2 , 32-63 μm , Pet. ether:EtOAc (12:1, 400 mL; 9:1, 120 mL; 9:2, 80 mL), 20 mL fractions. Fractions 33-45 were combined and the solvent evaporated under reduced pressure and the clear oil (which thickens and yellows in the presence of air) pumped under vacuum for 5 hrs.

Anal Calcd. for $\text{C}_{17}\text{H}_{28}\text{O}$; C, 82.20; H, 11.36. Found: C, 81.98, H, 11.16. (33% yield). IR (neat) 3333, 2927, 2857, 2257, 2161, 1467, 1427, 1378, 1324, 1163, 1061, 721 cm^{-1} . ^1H NMR (CDCl_3) δ 0.87 (t, $J = 6.5$ Hz, 3H), 1.19-1.4 (m, 10H), 1.33-1.40 (m, 2H), 1.40-1.74 (m, 2H), 2.15-2.29 (m, $J = 6.8$ Hz, 4H), 2.31 (s, 1H), 3.52-3.68 (t, $J = 6.1$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 14.39, 19.38, 19.57, 23.00, 25.06, 28.73, 29.21, 29.45, 29.60, 29.79, 32.16, 33.22, 62.67, 65.60, 66.18, 77.25, 78.16.

Phthalimido(heptadeca-5,7-diyne) (NB-78, NB-87, NB-157): To the alcohol (20g, 8.1 mmole) in a 3 neck r.b. flask equipped with a magnetic stirring bar and septa under argon, was added 60 mL of dry THF. Under a stream of argon, triphenylphosphine (2.53g, 9.7 mmole) and phthalimide (1.3g, 8.9 mmol) was added. The reaction mixture was stirred in a cold water bath and diethyl azodicarboxylate (1.52 ml, 9.7mmol) in an equal volume of THF was added dropwise over 10 min. The reaction mixture is allowed to warm to room temperature and stirred overnight. The solvent is then evaporated under reduced pressure and 50 ml of ether is added and the mixture placed in a freezer at -10°C overnight. The precipitated triphenylphosphine oxide is filtered off and the ether evaporated. Methanol (30 mL) is added and the solution then cooled again to -10°C . The product is then filtered off and recrystallized from cold methanol. (89% yield). mp $96-99^\circ\text{C}$. ^1H NMR (CDCl_3) δ 0.90 (t, $J = 6.6$ Hz, 3H), 1.29-1.36 (m, 12H), 1.51-1.68 (m, 6 H), 1.72-1.92 (m, 2H), 2.20-2.28 (m, 2H), 2.31-2.40 (m, 2H), 3.73 (t, $J = 6.9$ Hz, 2H), 7.73-7.81 (m, 2H), 7.84-7.96 (m, 2H). ^{13}C NMR (CDCl_3) δ 14.40, 19.19, 19.57, 23.00, 26.00, 28.15, 28.71, 29.21, 29.45, 29.61, 29.78, 32.22, 37.76, 65.59, 66.34, 76.78, 78.24, 123.56, 132.58, 134.23, 168.70. Analysis calcd for $\text{C}_{25}\text{H}_{31}\text{NO}_2$: C, 79.54; H, 8.27; N, 3.71; Found: C, 78.97; H, 8.29; N, 3.23.

1-Amino, heptadeca-5,7-diyne (NB-159)

Phthalimido(heptadeca-5,7-diyne) (NB-159) (2.72 g, 7.2 mmol) was placed in a flask fitted with a reflux condenser under argon. Methanol (40 ml) was added and then hydrazine monohydrate (0.33 mL). The reaction mixture was heated and refluxed for 5 hrs. It was then cooled to room temperature, hexane (20 mL) was added and a pink product (2.6 g), a combination of phthalimide and the desired product, filtered off. The pink product was soxhlet extracted with 50 mL of chloroform, the chloroform solution concentrated to 20 mL and filtered through celite and the solvent then evaporated to give the product as a waxy, low melting solid. IR (NaCl) 3333, 2920, 2850, 1634, 1553, 1444, 1336 cm^{-1} . ^1H NMR (CDCl_3) δ 0.87 (t, $J=5.6$ Hz, 3H), 0.97-1.51 (m, 12H), 1.51-1.60 (m, 6H), 1.93 (t, 3H), 2.10-2.23 (m, 4H), 2.74 (m, 2H). ^{13}C NMR (CDCl_3) δ 14.45, 19.39, 22.95, 26.01, 28.72, 28.72, 29.47, 29.64, 29.81, 32.23, 34.06, 41.57, 62.15, 65.56, 78.16, 128.82, 132.51.

Materials for Optical Limiting

The widespread use of lasers in both the commercial marketplace and in technologies manifests that there are diverse applications for these devices, but numerous safety concerns must be addressed.(1,2) These concerns involve the sensitivity of the human eye and certain electrooptic sensors to laser radiation, especially pulsed radiation. When lasers operating at a single frequency are involved, there are often materials that can offer adequate protection for that frequency, usually by reducing transmission. However, this approach is inadequate when multiple frequencies("agile frequency threat") are involved. Recent research in the application of organic and polymeric materials to optical limiting has largely focused on materials that exhibit the phenomenon of reverse saturable absorption(3). Materials that exhibit reverse saturable absorption have a relatively weak ground state absorption and a strong excited state absorption at the same wavelength. The metal phthalocyanines have been of particular interest in that intersystem crossing to a triplet state is facilitated.(1,2)

Given the interest in the use of materials related to phthalocyanines for optical limiting, we furnished samples of two related materials to Dr. T. Cooper and his colleagues and Wright-Patterson Air Force Base. The first material is a cyclotetramer derived from reaction of *p*-tricyanovinyl dimethylaniline(TCVDMA) with sodium propargyloxide in propargyl alcohol. The second material is the conjugated polymer that results from the interaction

of 4,5-dicyano-2-benzylidene-1,3-dithiole with Li *n*-butoxide or *n*-pentoxide in the corresponding alcohol. The molecular structures of the monomeric reactants are given in Figure 1.

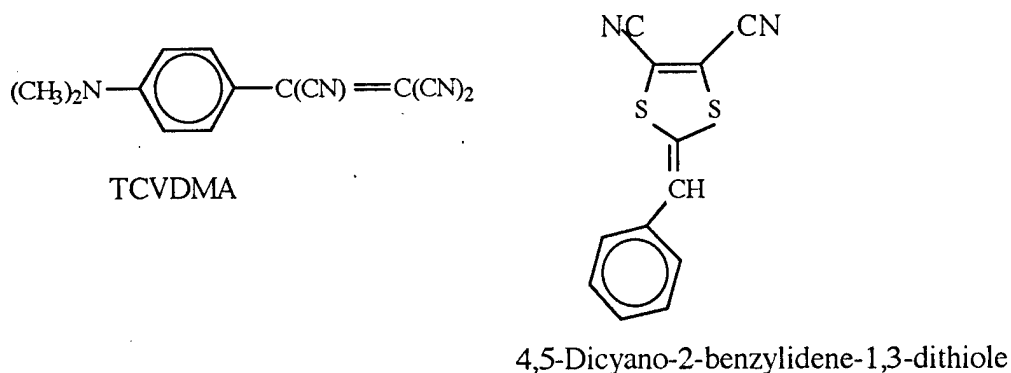


Figure 1. Molecular structures of monomers under investigation.

We were informed by Drs. Cooper and Natarajah of Wright Patterson that neither of these materials was an effective reverse saturable absorber.

Optical limiters that would function in the near infrared are presently of interest, and we were asked if we could supply materials that would reduce transmission in that wavelength region. Metal diselenolenes are known to be infrared absorbers(4) and their metal atoms and paramagnetism in certain cases may facilitate intersystem crossing to produce triplet states.(1,2)

A sample of the tetrabutylammonium salt of the Ni complex of *o*-benzenediselenolate(4) was synthesized and sent to the researchers at Wright Patterson. Dr. Natarajah at WPAFB has notified us that this salt functions as a reverse saturable absorber at 532 nm and that their evaluations in the near infrared are in progress.

EXPERIMENTAL SECTION

Cyclotetramerization of Tricyanovinyl dimethylaniline. To propargyl alcohol(2.3 ml) cooled in an ice bath was added sodium metal(60 mg, 2.5 gm atom). To this was added TCVDMA(280 mg, 1.26 mmole), and the mixture stirred in the ice bath for 2 3/4 hr. The mixture became brownish in color, and brine(20 ml) was added. A solid precipitate was isolated and air dried. , m.p. 196-200°(some decomp.; no gross decomp. to 304°. A blue solution in *o*-dichlorobenzene exhibited an absorption maximum near 650 nm. The infrared spectrum of the solid(Nujol) exhibited the following absorptions: 2210, 1605(s), 1585(s), 1500(s), 1405, 1330(s), 1280,

1205(s), 1150(s), 1080, 985, 955, 940, 880, 820(s), 785(w), 760, 750, 720, 675, 650 cm^{-1} .

Polymerization of 4,5-Dicyano-2-benzylidene-1,3-dithiole.
To *n*-butanol(5.6 ml) stirred magnetically under nitrogen in an ice bath was added methyllithium in ether(0.02 mole) via syringe; gas evolution occurred. When addition was finished, the ice bath was removed, and 4,5-Dicyano-2-benzylidene-1,3-dithiole(0.484 g, 2.0 mmol) was added with a gas over pressure. The reaction flask was heated in an oil bath at 110° for one hour under dynamic nitrogen. The mixture was allowed to cool and was mixed with 10% hydrochloric acid(25 ml). This mixture was extracted with chloroform(3-50 ml portions). The combined chloroform extracts were washed with 10% HCl(25 ml), brine(50 ml), and water(2 x 50 ml). The organic solution was dried over MgSO_4 , filtered and evaporated under reduced pressure. The residue was suspended in hexane/methanol(10:1) and filtered to give a purple-black solid (0.385 g), m.p. 205-207°(violet to black color change), no gross decomposition up to 330°. GPC analysis indicated a M.W. of 60,000 vs. a polystyrene standard. The FTIR spectrum exhibited the following(cm^{-1}): 2957, 2931, 1718, 1652, 1636, 1583, 1563, 1463, 1457, 1444, 1378, 1280, 1113, 1074, 1056, 695. The ^1H NMR spectrum(CDCl_3) exhibited the following: δ 6.91-7.57(multiplet, phenyl), 4.41(triplet, methylene), 4.05(singlet, methylene), 3.65(triplet, methylene), 1.20-1.75(multiplet), 0.78-1.08(multiplet). The ^{13}C NMR spectrum(CDCl_3) exhibited the following: δ 128.90-128.22, 19.0, 13.6. The electronic spectrum(CHCl_3 solution, 0.9 mg/25 ml) exhibited a broad maximum at 560 nm($A = 0.67$).

Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{S}_2\text{O}$ (repeat unit): C, 60.73; H, 5.10; N, 8.85; S, 20.27; O, 5.06. Found: C, 53.04; H, 4.61; N, 8.85; S, 20.05. The observed analysis corresponds to a repeat unit of $\text{C}_{14.1}\text{H}_{14.6}\text{N}_{2.02}\text{S}_{2.0}$.

Preparation of Tetrabutylammonium Nickel Bis(benzene-1,2-diselenolate. To a suspension of poly(1,2-phenylene diselenide)(4) (0.47g, 2 mmol) in methanol (10 mL) under argon and in an ice bath was added NaBH_4 in small portions until all of the polymer dissolved (0.25g, 6.6 mmol) giving an olive green solution. A solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.24g, 1 mmol) in methanol (10 mL) was added immediately, giving a black precipitate. After 1 hr at at 5°C, a solution of tetra butyl ammonium bromide was added and 5 min. later, the ice bath was removed. After 1.5 hr, the reaction mixture was filtered to give a black precipitate which was washed with

methanol. The filtrate was concentrated under vacuum and left under argon overnight after which burgundy crystals and a colorless filtrate were obtained. These crystals (NB-104B) were filtered off, washed with ethanol and dried. The crystals were purified by dissolving in a small amount of methylene chloride, filtering the solution through celite and evaporation of the solvent under reduced pressure to give the desired product as black flecks.

NB-104B (black crystals), mp 189-190.5 °C(lit.(4) m.p. 192°C); 0.25g. UV-Vis. (CH₂Cl₂) (391 nm, 847 nm, 965 nm) in agreement with the literature(4).

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V. Shivshankar, C. Sung, J. Kumar, S.K. Tripathy, and D.J. Sandman, "Anisotropic Surface Eruptions on Polymerized Diacetylene Crystals", Acta Polymerica, **48**, 88-91(1997).

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S. Balasubramanian, X. Wang, H.C. Wang, L. Li, D.J. Sandman, J. Kumar, S.K. Tripathy, and M.F. Rubner, "Acentric Self-Assembly of an Azo Polymer Through Layer-by-Layer Deposition", Polymer Preprints, **38(2)**, 502-503(1997).

List of Personnel

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Postdoctoral Researcher: Dr. Nicholas Benfaremo

Graduate Students: V. Shivshankar, Hyunjoo Moon, Zo-Hong Tsai, Xinli Jiang. Ph.D. degrees were awarded to V. Shivshankar and Xinli Jiang. The M.S. degree was awarded to Hyunjoo Moon.

Interactions/Transitions

Papers presented at meetings:

"ATOMIC FORCE MICROSCOPY STUDIES OF DIACETYLENE MONOMERS AND POLYMERS", V. Shivshankar, C. Sung, J. Kumar, S.K. Tripathy, and D.J. Sandman, American Chemical Society Spring National Meeting, New Orleans, Louisiana, March 24-29, 1996; Abstracts of Papers PMSE 243.

V. Shivshankar, C. Sung, J. Kumar, S.K. Tripathy, and D.J. Sandman, "Chromic transitions in Urethane-Substituted Polydiacetylenes: Bulk and Surface Effects" International Conference on the Science and Technology of Synthetic Metals(ICSMT '96), Snowbird, Utah, July 28-August 2, 1996; Paper P3.141, Abstracts, p. 369.

"CHROMIC PROPERTIES AND THE SURFACE MORPHOLOGY OF POLYDIACETYLENES" V. Shivshankar, C. Sung, J. Kumar, S.K. Tripathy, and D.J. Sandman, American Chemical Society Fall National Meeting, Orlando, Florida, August 25-29, 1996; Abstracts of Papers PMSE 81.

"PROGRESS IN CHROMIC URETHANE-SUBSTITUTED POLYDIACETYLENES" D.J. Sandman, V. Shivshankar, J.C. Stark, N. Benfaremo, Z.-H. Tsai, C. Sung, , S.K. Tripathy, and J. Kumar American Chemical Society Fall National Meeting, Orlando, Florida, August 25-29, 1996; Abstracts of Papers PMSE 120.

Materials Research Society 1996 Fall Meeting, Boston, Massachusetts, December 2-6, 1996, Symposium D: "Properties and Applications of Electronic Organic Materials and Fullerenes"

"NEW CHROMIC POLYDIACETYLENE CRYSTALS" N. Benfaremo, J.C. Stark, V. Shivshankar, J. Kumar, and D.J. Sandman, Paper D7.18.

"RADIATION DOSE RATE DEPENDENT SURFACE MORPHOLOGY OF CHROMIC POLYDIACETYLENE(PDA) SINGLE CRYSTALS" V. Shivshankar, C. Sung, J. Kumar, S.K. Tripathy, and D.J. Sandman, Paper D14.6.

"NEW POLYDIACETYLENES WITH VISIBLE CHROMOPHORIC SIDE GROUPS" J.L. Foley, V. Shivshankar, and D.J. Sandman, Paper D14.7.

Materials Research Society 1997 Fall Meeting, Boston, Massachusetts, December 1-5, 1997, Symposium J: "Electrical, Optical, and Magnetic Properties of Organic Solid-State Materials IV", abstracts submitted: "SELF-ASSEMBLING FUNCTIONALIZABLE POLYDIACETYLENES AND THEIR OPTICAL PROPERTIES" M. Sukwattanasinitt, X. Wang, D.-C. Lee, L. Li, J. Kumar, S.K. Tripathy, and D.J. Sandman
"OPTICAL PROPERTIES OF DISTYRYLBENZENE CHROMOPHORES AND THEIR SEGMENTED COPOLYMERS" N. Benfaremo, D.J. Sandman, S. Tripathy, J. Kumar, K. Yang, M. Rubner, and C. Lyons.
"NEW POLYDIACETYLENES WITH VISIBLE CHROMOPHORIC SIDE GROUPS" J.L. Foley, V. Shivshankar, and D.J. Sandman.

Invited Lectures presented by D.J. Sandman:

1. University of Connecticut, Storrs, CT February 7, 1997, "Side Chain Processes in Polydiacetylenes"
2. XIII International Conference on the Chemistry of the Organic Solid State, State University of New York at Stony Brook July 13-18, 1997: "The Crystal Structure-Linear Spectroscopy Relationship for Polydiacetylenes and Related Issues", plenary lecture.
3. Fifth Chemical Congress of North America, Cancun, Mexico, November 11-15, 1997: "The Crystal Structure-Linear Spectroscopy Relationship for Polydiacetylenes and Related Topics", in the Symposium on Polymers from Acetylenic Compounds.

Invited Lecture presented by V. Shivshankar:

"CHROMIC PROPERTIES AND THE SURFACE MORPHOLOGY OF POLYDIACETYLENES" V. Shivshankar, C. Sung, J. Kumar, S.K. Tripathy, and D.J. Sandman, American Chemical Society Fall National Meeting, Orlando, Florida, August 25-29, 1996; Abstracts of Papers PMSE 81. This lecture was presented in the Sherwin Williams Student Award Symposium in Applied Polymer Science

Transitions: New materials for evaluation in optical limiting were synthesized and sent to Drs. Cooper and Natarajah at Wright Patterson Air Force Base.