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Conference Report

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A Topical Workshop entitled "Organic and Polymeric Nonlinear optical Materials", sponsored by the Division of Polymer Chemistry of the American Chemical society was held from May 16-19, 1988 in Virginia Beach, VA. The workshop was organized and chaired by Diana Gerbi of the 3M Company and by Sukant Tripathy of the University of Lowell. It was attended by over 80 participants and consisted of 18 lectures and about 10 poster presentations.

The meeting was held in a most pleasant surrounding at the Cavalier Hotel in Virginia Beach. It started with the welcoming reception on Monday evening; Thursday evening the formal banquet of the Workshop was held.

The Workshop on "Nonlinear Optical Properties" was a most welcome undertaking and very timely; it helped the participants to understand all the intricate problems that are associated with the nonlinear optical (NLO) properties of organic as well as of polymeric materials. A general hope was expressed that successful applications will be found, especially for polymeric materials; many theoretical considerations and model compound studies that are presently underway are expected to promote understanding of the overall phenomena of NLO in NLO active materials and their application in various devices.

The field of nonlinear properties, particularly nonlinear optical properties of, polymeric materials is in the embryonic stage of a rapidly advancing development. The purpose of the Workshop was to define the possibilities of where NLO materials could be used and how NLO molecular structures actually could be designed and prepared in a useful form.

Since the field is still in its beginning stage of development, it was dominated by discussion of the physics of the NLO phenomena and by theoretical considerations. Possible applications of the NLO materials for various device applications were also discussed.

The Workshop was opened on Tuesday morning by D.R. Ulrich who presented "An Overview on Nonlinear Optical Polymer Systems and Devices".

The opening speaker asked the question: "Why study properties of NLO materials and especially why NLO active polymers?" It was suggested that many advantages might be expected from polymeric materials. They would have subpicosecond response times, large nonresonant non-linearities, low DC dielectric constants, low switching energy, broadband performance, low absorption, absence of diffusion problems, potential for (UV to Near-IR) resonance enhancement, ease of processing by synthesis modification, possibly room temperature operations, environmental stability, and mechanical and structural integrity. The NLO response in polymers can be viewed on the molecular level: on the microscopic polarization relating to applied electric field and on the microscopic NLO properties which originate from the polarization response of molecular electrons. The polarization of the electrons depend on: $\chi(1)$—which represents linear optics, $\chi(2)$ the second order response, i.e. second harmonic generation, optical rectification, and $\chi(3)$ which represents the third order nonlinear process, i. e., third harmonic and four wave degenerate mixing.

NLO polymers (as far as $\chi(2)$ is concerned) have great potential for optical signal processing (optical computing), as neutral networks, and as spatial light modulators. In all optical applications (where $\chi(3)$ is important), NLO polymers show promise in signal processing, either in series, such as in wave guides, or in parallel plane wave configuration. They also have potential for tunable filters, sensor protection, phase conjugation, and optical switches. D. Ulrich discussed various aspects of the comparison of optical switching technologies, optical performance and the mechanisms of four wave mixing. He pointed out the research directions of NLO properties in the polymer requirements, particularly for the importance of nonlinear susceptibilities. He pointed out the potential ease of processing of polymeric materials and the great need for thin films of reasonable optical quality both in terms of transparencies ($A<0.1$/cm); optical loss in a waveguide [≤1 dB/cm] and smooth surfaces, environmental stability and the low switching energy that might be needed for picojoule and diode lasers. Mention was made of the status of the known NLO active polymer classes. Isotropic polymers, bond alternation polymers, liquid-crystalline polymers, rigid rod

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aromatic heterocyclic polymers and polydiacetylenes have been identified with such characteristics.

Isotropic polymers include poled glasses, guest-host and blends. Electrically poled pendant side chain polymers (PMMA with side chain NLO mesogen) show best second order and E-O activity so far. They have SHG $\chi(2)$ equivalent to or better than $LiNbO_3$ and an E-O coefficient $r \leq LiNbO_3$. As slab waveguides, performance at 1 GHz has recently demonstrated NLO polymers are not restricted by high dielective constant and Curie temperature operation (to obtain the highest resonant $\chi(2)$ like $LiNbO_3$). As a result performance to 100 GHz is predicted. Only the electrodes in waveguides are the limiting factor. $LiNbO_3$ is limited to 8-24 GHz. KTP, potassium titanyl phosphate, is a new oxide crystal which shows higher SHG efficiency than $LiNbO_3$, but has a low laser damage threshold. The poled polymers show damage thresholds of 1 GW/cm and better. The Air Force has let development contracts for high efficiency laser doublers and Mach-Zehnder modulators. One interest is for 20 GHz radar signal processing.

Bond alternation polymers are ladder polymers and pristine conducting polymers such as polyacetylene. Vinylamine and BBL ladder polymers have now been reported with $\chi(3)$ in the range of 10^{-9} esu. One year ago the best polymers showed 10^{-11} esu and a few 10^{-10} esu. For marginal device application such as for optical shutters third order $\chi(3)$ of 10^9 esu was required. For use as etalons, which would be a major step toward optical neural nets for optical computing at least 10^7 is required.

Another major step has been the discovery to bleach out bands in the visible of the ladder polymers and shift them to the near IR. This is done by doping the ladder polymers which also increases $\chi(3)$ in preliminary measurement; the doping causes a charged lattice (bipolaron). These are candidates for optical limiters for vision protection against laser battlefield threats.

Liquid crystalline polymers are of interest for both second and third order effects. The rigid rod polymers, polybenzothiazole and polybenzoxazole, PBT and PBO, respectively, show good $\chi(3)$ in biaxial films. Polyphenylvinylene, PPV, recently showed $\chi(3)$ of 10^{-10} esu and is a candidate for NLO polarization bistability and birefringent devises along with PBT.

Metallated macrocylces such as silicon napthalcyanine and phthalocyanine have recently been shown to have near-resonant $\chi(3)$ of 10^{-6} esu, which is approaching the resonant values of galliumaluminum arsenide (GaAlAs) multiquantum wells. The macrocycles have electronic bistability responses in the nanosecond regime. Their performance has been demonstrated in Fabret-Perut etalons, which are frequency selectors.

It was pointed out that in polymeric systems there seems to be no need for units of conjugation longer than 50 to 60Å or 20 to 25 monomer repeat units.

P.N. Prasad of the State University of New York at Buffalo presented his talk on "Nonlinear Optical Effects in Polymeric Films". He suggested that the predictability of polymer structures for molecular engineering is reasonable and that large $\chi(2)$ with fast response time and low DC dielectric constant have already been achieved. Guided wave devices have been demonstrated with polydiacetylene in Langmuir Blodgett films; $\chi(3) = 10^{-9}$ esu has been achieved. Polymers seem to be desirable from the material processing and device application points of view; doped polymers and liquid crystalline polymers are primary candidates. Many devices can be visualized, and planned in concept but are restricted by inorganic crystal and semiconductor materials limitations.

For measurements of $\chi(3)$ there are a number of important and relevant parameters: the magnitude of $\chi(3)$, the response time, the anisotropy of $\chi(3)$, the sign of $\chi(3)$, local field effects, electronic resonance enhancement, and vibrational resonance enhancement. Polymers most studied in this group were phthalocyanines, polythiophenes, liquid crystalline rigid rod polymers, side chain liquid crystalline polymers, polyacetylenes and specifically designed derivatives of methacrylates.

"Recent Advances in Nonlinear Optical Properties of Organic and Polymer Systems" was the subject of a talk by A.F. Garito, of the University of Pennsylvania. He discussed in great detail the electron correlation and resonance processes; he pointed out that the π-electron states of organic molecules are dominated by electron correlations. Octatetraene was particularly mentioned as a subject in his detailed studies; it included such factors as the transition density matrix diagram and the study of the dependence of gamma on the number of sites, but also the microscopic origin of gamma for various polyenes. The dependence of gamma on the chain length of the polymer was also discussed, not only for regular dienes but also for the NLO susceptibility of other conjugated chains. These were shown to apply to liquid crystalline rigid chain polymers (PBT and PBO).

This talk was followed by a lecture by S. Etemad of Bell Communications who spoke on "Conjugated Polymers and Nonlinear Optics". He presented and discussed the behavior of the various structures of polyacetylenes and their behavior; particularly the properties of trans-polyacetylene were discussed. Among other things, S. Etemad mentioned the chemist's or chemistry's view of the high correlated states, and he focused on finite polyene structures of polyene units involving limited conjugation lengths, the Coulomb interactions in terms of the perturbation approach and the highly correlated states. He also emphasized the third harmonic generation and the effect of soliton doping; it involves the appearance of absorption bands near the mid-gap and the appearance of enhanced IR active local modes, but no increase in $\chi(3)$. Specifically the trans-polyacetylene structure was investigated in the form of Durham samples; the solubilized samples and the Shirakawa material was investigated.

In the afternoon of Tuesday, May 17 four lectures were scheduled. The first presentation was by Alan J. Heeger of the University of California at Santa Barbara; the title of his talk was "Anisotropy of the Third Order Nonlinear Optical Susceptibility in Conjugated Polymers". He also discussed the NLO properties of polyacetylene and described the different molecular as well as electronic structures involving charge transfer exitons, which ultimately can be transformed into a NLO type material. Heeger pointed out (by using trans-polyacetylene as the example) that the broken trans-polyacetylene symmetry with a twofold degenerate ground state of the bond-bond alternational domain, or soliton and the "instantons" as the source of $\chi(3)$ in trans-polyacetylene. The instantons are nonlinear zero point fluc-

tuations obtained by the photoproduction of charged solutions; Heeger concluded that direct photogeneration of solutions can be obtained with the help of ground state fluctuations; he gave examples where resonance processes (excitons, solitons and polarons are involved) existed and compared them to non-resonant processes. Heeger also concluded that solutions can lead directly to resonance; the non-resonance is caused by instantons. Three photon resonant processes were characterized (in the level of 0.4 to 0.6 electron volts) in the trans-polyacetylenes spectrum.

Poly(p-phenylenevinylenes) were also discussed. These structures have a high molecular weight and large gaps; they can form oriented films from water soluble precursors. Heeger concluded that large $\chi(3)$ is a general feature of conjugated systems and that the nonlinearity is associated with the π-electrons from rigid bandstructures.

"Nonlinear Optics in Ordered Molecular Systems" was the subject of a presentation by K. D. Singer of the AT&T Engineering Research Center, Princeton. Singer compared molecular materials in terms of macroscopic polarization, microscopic polarization and Van der Waal's materials. He compared crystals, Langmuir-Blodgett films, smectic and nematic liquid crystals, and oriented order in isotropic liquids. He paid particular attention to the electric field poling where low molecular weight polarizable materials are immersed into either a liquid or a glassy material. Poling can be carried out under uniaxial stress which affects the second harmonic tensor properties and the molecular distribution. He mentioned new polymer materials that had been subjected to Corona poling. Particular emphasis was placed on trans-azo compounds with a nitro-group on one end of the aromatic molecule and substituted amino groups on the other. Tricyanoethylenes were used on one end and the dialkylamine group on the other end of the molecules; they were also substituents on trans-stilbenes; second-order molecular polarizabilities, Bu up to $4,0 \times 10^{-30}$ $\beta\mu$,cm^{5}D/esu were obtained. AT λ of 1.36 to 1.58 μm.

H. Nakanishi of the Research Institute for Polymers and Textiles, Tsukuba, Japan presented his work on "Several Series of Novel Polydiacetylenes for Nonlinear Optics". His work primarily involved polydiacetylenes. Diacetylenes substituted with aromatic rings on either side of the diacetylene groups were polymerized and the properties of their polymers studied. Nakanishi discussed in great length the preparation of the monomers and their polymerization and found that in many polydiacetylenes the $\chi(3)$ values of thin films were in the neighborhood of 10^{-9} to 10^{-10}esu. Polydiacetylenes with n-butyl-tetrafluorophenyl-groups have values 10 times higher.

The final talk of the first day was presented by F. Kajzar, of the CEA-CENS, Gif Sur Yvette, France on "Resonance Effects in Cubic Hyperpolarisabilities of Conjugated Polymers". He described the Langmuir-Blodgett method of thin film preparation, again based on polydiacetylenes. Other methods that were used for the preparation of these thin monocrystalline films were solution casting, dipping techniques from polymer solution, evaporation techniques, sublimation, and shear techniques. Thin films (0.003 microns up to a few 0.1 microns) were obtained. The principle importance of these LB films is that they are centro-aymmetric films with controllable thickness. When the thickness was limited to a few thousand Angstroms there was a two dimensional order. Problems existed because of the formation of free polycrystallites. Even solution casting gave similar problems; in addition large surface roughness was encountered. Dipping techniques, epitaxial growth and monomer deposition by sublimation at 10^{-6} Torr followed by polymerization was also discussed. It was concluded that advantages in some of these methods have been encountered with large $\chi(3)$, fast response times and two photon absorption processes leading to broadband transparency. Thin film feasibility by different techniques and oriented thin films expitaxy were obtained for communication windows, active optical path stability and logic systems. Optical and physical-chemical properties of the polymers could be modified by proper selection of their side groups. Problems have been noticed in some cases with polyacetylenes: light scattering, photodecompositon, limited chemical stability and the blue-red transformation.

On Wednesday, the morning session was opened by Y.R. Shen of the University of California at Berkeley on "Nonlinear Optical Measurements on Liquid Crystals and Quasi-Liquid Crystals". Shen pointed out that the motivation for this work was the observation that liquid crystalline molecules are highly nonlinear, that the existence of liquid crystals with different molecular structures are known and that the nonlinearities were found to depend on their molecular structure. He particularly pointed to the fact that interesting material properties could be measured when molecular monolayers were spread on water. The advantages are that the molecular density can be variable and that the local field effects could therefore be less important. This method has the disadvantages that not all molecules are spreadable in water, and some molecules could interact with water. The author worked particularly with alkyl-cyanopolyphenyls and the corresponding pyrimidines. Large second order polarizabilities in such molecules were observed; it was concluded that the nitrile group acted as an electron withdrawing group more effectively than the carboxylic acid group. Interruption of the electron localization decreases by $\chi(2)$. The triphenyl group was found to have lower susceptibilities than the biphenyl moity presumably because of the twisting between phenyl rings decreases the pi-orbital overlap.

Nonlinearities of hemicyanine dyes were also studied. Protonation in these dyes plays an important role in their behavior; it was found that it surpressed the charge transfer absorption substantially, which drastically reduced $\chi(2)$; the UV-absorption band has little effect on $\chi(2)$. A very interesting group of compounds were the spiropyrans which can be easily transformed by photo-excitation into merocyanines, the latter having relatively high $\chi(3)$ values.

"Nonlinear Optical Effects in Conjugated Systems" was the subject of a presentation by D.J. Gerbi of the 3M Company. She described the utilization of materials on the basis of $\chi(2)$ in optical communications such as in fiber optics, telecommunication and possibly utilizating of $\chi(3)$ in signal processing such as in all-optical information processing, imaging technologies and as sensors in fiber optics. Initially the compounds that are suspected as being NLO active were studied as powders because the second harmonic generation (SHG) can be determined with microcrystalline powders by the Kurtz Powder Method, and compared with urea. This technique is useful for screening but cannot resolve micro-

and macroscopic contributions to nonlinearity. Single crystal SHG measurements requires large noncentro-symmetric single crystals, but measures more accurately the tensor elements $\chi(2)$; it required, however, crystal orientation and the indices of refractive index must be balanced. Efish measurements were also carried out under an electric field. These measurements were done in solutions of low polarity solvents; molecular properties were obtained but these properties were subject to the electron environment. Polymer poling, or orientation of the dipoles in the polymer matrix by an electric field were measured directly on polarizable polymer systems. It was pointed out that the advantage of organic materials are: Good synthetic approaches via the use of delocalization substituents, subpicosecond response times, transparency, mechanical and structural stability, high radiation damage threshold, environmental stability, processability, and room temperature operation of the devices. Potential applications for SHG are in wave guides and optical disks, utilizing the electro-optical effects in modulator and direct couplers. Particularly studied were derivative and various isomers of chloro-nitroaniline.

G.R. Meredith of E.I. du Pont de Nemours and Co. gave his presentation on "Optical Nonlinearity: Molecules, Assemblies and Wave Phenomena".

The last talk of the morning session was by G. Khanarian "Characterization of Polymeric Nonlinear Optical Materials". His group has been studying the types of molecular packing and linear polarizability of bi- and terphenyls with a nitro-group at one end of the molecule and an amino group on the other; poling of these materials in dipolar polymers was primarily investigated. Of particular importance was the study of NLO side chain polymers with NLO active groups separated from the backbone of the polymer chain with flexible spacer groups. The dependence of the glass and clearing temperature on the length of the methylene spacer groups was investigated and the properties were described in terms of $\chi(2)$; Langmuir-Blodgett film formation was also studied.

In the afternoon of Wednesday, May 18, T. Richardson of the University of Oxford, U.K. spoke on "Preparation and Characterization of Organo-Transition Metal Langmuir-Blodgett Films". He described a series of novel ruthenium compounds which have been developed for the use of Langmuir-Blodgett techniques. Complexing of a ruthenium as the head group to a cyanoterphenyl, liquid crystalline molecules have been shown to increase the NLO hyperpolarizability and to induce multilayer formation. Optical absorption data have revealed excellent reproducibility of successful monolayer transfer. A second harmonic generation was observed; the effect could be increased by incorporation of substituted liquid crystalline molecules into the void between the terphenyl chain and the adjacent ruthenium-substituted molecules. Furthermore, the NLO response has been optimized by systematically varying the electro-releasing groups and the conjugation within the molecule.

"Optical Properties of Organized Assemblies" was discussed by S.K. Tripathy of the University of Lowell. The author studied diacetylene derivatives as the backbone responsible for the optical and NLO properties. Specific side groups were used as substituents to provide a handle to control the structure and facilitate the fabrication of the materials. Selected conjugated macromolecular systems that were capable of organizing in mono-and multilayer assemblies were investigated. Their microstructures and morphologies were characterized, and the anticipated electronic and optical properties were measured. Effects of substituents on the polydiacetylenic electronic structures were also investigated with typical molecular structures that are known for their potential NLO properties; polypyrroles were also investigated.

"The Nonlinear Optics of Langmuir-Blodgett Films" was also the subject of a talk by I. Peterson of GEC Research, Ltd., U. K. Peterson described molecular structures based on p-nitroanilines and merocyanine, in monolayer formation. The measurement of the refractive index on the surface plasmon $\chi(2)$ was done by attenuated total reflection. $\chi(2)$ was found to depend very much on the morphology obtained based on the sample preparation.

Wednesday evening was reserved for a poster session which consisted of 10 posters on the following subjects: "Optical Kerr Measurements on some Ferrocene Derivatives by C.S. Winter, J. D. Rush, and S.N. Oliver from the British Telecom Research Labs and the Jet Propulsion Laboratory; "Theoretical Models for the Second Hyperpolarizability of Novel Conjugated Polymers" by D.N. Beratan of the Jet Propulsion Laboratory; "Nonlinear Optical Properties of Transition Metal Poly-ynes" by E. A. Chauchard, M.P. Cockerham, P.L. Porter, S. Guha, C.C. Frazier from the Martin Marietta laboratories. "Reverse Saturable Absorbers: Indanthrone and Its Derivatives" by R.S. Potember, R.C. Hoffman, and K. A. Stetyick of the Johns Hopkins University, "The Preparation and Characterization of Polymeric Materials with Enhanced Second Order Nonlinearities" by M.L. Shilling, H.E. Katz, and D.I. Cox, AT&T Bell Laboratories, "Second Harmonic Generation in Doped Glassy Polymer Films as a Function of Physical Aging" by H.L. Hampsch, J. Yang, G.K. Wong and J.M. Torkelson of Northwestern University, "Electro-Optic, Polymer Clad, E-Field Sensor" by L. M. Hayden and G. F. Sauter of the UNISYS Corporation, "Molecular Conformation and the Stability of Tict State in P, P'-Disubstituted-l, 6-Diphenyl-l, 3, 5-Hexatrienes" by C.T. Lin, H.W. Guan, R.K. McCoy and C.W. Spangler of Northern Illinois University, "Second and Third-Order Nonlinear Optical Properties of End-Capped Acetylenic Oligomers" by J.W. Perry, A.E. Stiegman, S.R. Marder and D.R. Coulter of the Jet Propulsion Laboratory, "Optical Field Induced Scattering in Polymer Dispersed Liquid Crystal Films" by P. Palffy-Muhoray, M.A. Lee and J.L. West of Kent State University, "Fabrication of Waveguide Structures From Soluble Polydiacetylenes" by G.L. Baker, N.E. Schlotter, J.L. Jackel, P. Townsend, S. Etemad of the Bell Communication Research Laboratory.

The session on Thursday morning, May 19 was opened by R.S. Lytel of Lockheed Research and Development on "Advances in Organic Electro-Optic Devices". The major benefits of NLO organic/polymeric materials were discussed. Especially emphasized was the large nonresident response and the speed of the response. The author pointed out the importance of polymeric materials as potential candidates for a number of device applications that are in various stages of conception, preparation and utilization.

This lecture was followed by a talk on "Organic Nonlinear Optical Devices and Material Considerations" by B.K. Nayar of the British Telecom Research Laboratories, U.K. Laser

spectroscopy in polymers allows the study of energy diagrams of polymers and of various dye molecules with their photophysical and photochemical bleaching capabilities.

Additional work on polydiacetylenes was described; the conjugation length of the diacetylene units has been estimated from the planarity of the chain backbone. It was found that the increase of the chain length of the polydiacetylene molecules does not guarantee the increase of the conjugation length. Polydiacetylenes are known to exist in allylic and acetylenic forms but the acetylenic form is predominant in these polymers. Much emphasis in this work was also placed on the growth of thin film and single crystals by various methods. Polyacetylenes with various R groups on the diacetylene units were studied to introduce the appropriate optical characteristic together with fabricability.

The workshop was concluded by talks by M. Thakur of AT&T entitled "Toward Nonlinear Optical Applications of Polydiacetylenes" and by D. Haarer of the University of Bayreuth, Federal Republic of Germany on "High Resolution Laser Spectroscopy in Polymers".