The research conducted under this contract focused on the molecular mechanics of polymeric films in relation to their ultrastructure and nonlinear optical properties aimed towards eventual applications in integrated optical and microelectronic devices. Several landmark results were obtained. They are: (i) First demonstration of femtosecond response of nonresonant optical nonlinearity in conjugated polymers. (ii) First demonstration of third-harmonic generation from a monolayer film of a conjugated polymer. (iii) First case of a conformational transition in a monolayer film of a conjugated polymer. (iv) First picosecond coherent Raman scattering study of a polymeric system.

Our studies of third order optical nonlinearities using picosecond and subpicosecond degenerate four wave mixing as well as third harmonic generation established clearly a strong dependence of $\chi^{(3)}$ on the effective $\pi$-electron conjugation. Our study of...
vibrationally resonance enhanced nonlinearity using coherent Raman scattering
revealed an enhancement by two orders of magnitude with response still in
picoseconds.

The Langmuir-Blodgett method was applied for the preparation of monolayer
and multilayer films of several types of polydiacetylenes. Our study showed
that the Langmuir-Blodgett technique can successfully be used for molecular
engineering of ultrathin polymeric films with monomolecular control. Other
techniques used for the preparation of ultrathin polymeric films were electro-
chemical polymerization and gas-solid interface reactions.

For the characterization and the study of ultrastructure of polymeric films
several new methods were used. The picosecond transient grating method of
generating ultrasonic phonons was used to study the acoustic speed and attenuation
in a polystyrene film. A novel application of quartz crystal microbalance was
demonstrated for studying the Langmuir-Blodgett films. We also used the technique
of laser Raman optical waveguide to obtain the vibrational spectra and hence probe
the ultrastructure in monolayer films of several polydiacetylenes. Inelastic
electron tunneling spectroscopy was also successfully used for the study of
polymeric films.
FINAL REPORT

PROJECT: Molecular Mechanics of Polymeric Interactions

SPONSOR: USAFOSR

PERIOD: February 15, 1985 to April 14, 1987

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Significant research was accomplished in the following areas: (1) study of non-linear optical effects in polymeric materials, (ii) study of structure and dynamics of Langmuir-Blodgett films, (iii) electrochemical preparation and structural characterization of electroactive polymeric films, (iv) polymers produced by gas-solid interface reactions, (v) inelastic electron-tunneling spectroscopy of submicron thin polymeric films.

For the study of nonlinear optical effects in polymeric materials, both pico- and nanosecond laser systems were used. Our picosecond and subpicosecond experimental arrangement uses a CW mode-locked Nd-Yag laser (Spectra Physics model 3000) pumped dye laser. The pulses are subsequently amplified.

For picosecond transient grating experiment (two-fold degenerate pump-probe four wave mixing experiments), beams from both amplifiers were used. Using the picosecond laser system we conducted, to our knowledge, the first picosecond transient grating study of pure and mixed polymeric films of micron dimensions. Picosecond transient grating experiments were performed on a 5μ thick pure polystyrene film at room temperature. In both cases, the observed acoustic modulation of the diffracted signal was explained by the formation of a thermal grating. No detectable acoustic attenuation was observed within the time delay of 6 nanoseconds, and the speed of sound obtained from the acoustic modulation period is in excellent agreement with that reported by an ultrasonic measurement. The zero-time delay coherent third-order nonlinear electronic response was found to be shorter than 2 ps. This work is already published¹.

Using pico- and nanosecond set-up in a degenerate four wave mixing arrangement, we have measured electronic third-order optical nonlinearity ($\chi^{(3)}$) for two systems which are representative of two classes of polymers. The first
class of polymer is polydiacetylenes. Here we have investigated a specific polydiacetylene, poly-4-BCMU, which undergoes a red-to-yellow conformational transition at high temperature. The conformational transition changes the $\pi$-electron conjugation which is considerably reduced in the yellow form. Also, poly-4-BCMU is a soluble polydiacetylene, therefore, can easily be cast as a film. A 4 $\mu$m thick film of poly-4-BCMU was cast on a microscopic slide from a chloroform solution. The film at room temperature is in the red form. With the shortened pulse, the DFWM signal obtained from the red form exhibits a response of ~700 fs which is shorter than the autocorrelation width. A similar result is obtained for the yellow form. Therefore, the subpicosecond response of the electronic $\chi^{(3)}$ in conjugated polymeric systems was established for the first time. In order to obtain the value of $\chi^{(3)}$, a comparative study with CS$_2$ was conducted. The values obtained are $\chi^{(3)}_{1111} = 4 \times 10^{-10}$ esu for the red form and $\chi^{(3)}_{1111} = 2.5 \times 10^{-11}$ esu for the yellow form and they are comparable for wavelengths 585 and 605 nm. No significant change in the value of $\chi^{(3)}$ is found as the film is rotated indicating that it behaves isotropically. A 16-fold change in the value of $\chi^{(3)}$ in going from the red form to the yellow form with reduced conjugation demonstrates the dependence of $\chi^{(3)}$ on $\pi$-electron conjugation. Using a one-dimensional pseudopotential model for conjugated $\pi$-electron system, the $\pi$-electron contributions to $\chi^{(3)}$ are estimated to be $9 \times 10^{-12}$ and $1.5 \times 10^{-12}$ esu for the red and the yellow forms respectively. This work has been published$^2$.

The second class of polymer is a conjugated aromatic heterocyclic polymer, poly-p-phenylenebenzobisthiazole (PBT) which has a very high mechanical strength due to its rigid rod conformation as well as environmental stability and a high laser damage threshold. The measurement
in a 33μm thick as-spun biaxial film of PBT yields $\chi^{(3)}_{1111} = 9 \times 10^{-12}$ esu. Again, a subpsecound response for the $\chi^{(3)}$ is found. The measurements at two wave lengths suggests that they are non-resonant $\chi^{(3)}$ values. The measured anisotropy of $\chi^{(3)}$ as a function of angular orientation of the film at two different sets of laser polarization is explained by using the fourth rank tensor properties of $\chi^{(3)}$ and assuming an orthorhombic symmetry for the PBT biaxial film. This study has been published\(^3\).

We have also used nanosecond degenerate four wave mixing experiments to study the rod-to-coil transition in the toluene solution of poly-4-BCMU. We used both excimer-pumped-dye laser and the second harmonic of a Nd-Yag laser for this experiment. The principal wave length used was 532 nm. In the first experiment, we used two pump beams at 532 nm from the excimer pumped dye laser. The third beam, the probe, was the second harmonic of a Nd-Yag laser and was applied at varying time delays with respect to the pump beams. The Bragg diffracted signal was plotted as a function of the time delay. The delay time was found to be of the order of ~10 μs, which was consistent with the theoretically predicted value for a thermal grating. We monitored the change in intensity of this thermal grating as a function of temperature. The intensity drops as the polymer undergoes phase transition. The observed intensity changes are in good agreement with the theory of chain folding to lead to a rod-to-coil transition. In the high temperature coil form, which is yellow, 532 nm pulses do not form any thermal grating but 460 nm excitation forms a weak thermal grating. This work is published\(^4\).

Vibrational resonance can increase $\chi^{(3)}$ of a system. Vibrational resonance of $\chi^{(3)}$ can be mapped out in a coherent Raman scattering experiment such as CARS and CSRS. Thermal effects generated by Raman
scattering (vibrational resonance) can be expected to be much smaller than that observed for an electronic resonance. Time response of vibrationally resonance enhanced $\chi^{(3)}$ is determined by vibrational dephasing which can be measured by time-resolved coherent Raman spectroscopy experiments. Although frequency resolved CARS and CSRS experiments have been conducted for polymers both in forms of films and solutions, to our knowledge no time-resolved study of these processes in polymeric systems has been reported.

We have conducted both time-resolved and frequency domain CARS and CSRS studies of a polymeric system to investigate vibrational dephasing processes. The system selected for this study was poly-4-BCMU. This conjugated polymeric system exhibits a large $\chi^{(3)}$ as determined by degenerate four wave mixing described above. The large value of $\chi^{(3)}$ permitted us to conduct CARS and CSRS studies in a polymeric film which is only a few microns thick.

For CARS and CSRS experiment, pulses $\omega_1$ (17076 cm$^{-1}$) and $\omega_2$ (15544 cm$^{-1}$) were used from two separate amplifiers described above. The signals were detected at $\omega_3 = 2\omega_1 - \omega_2$ in case of CARS, and at $\omega_3 = 2\omega_2 - \omega_1$ in case of CSRS. For time-resolved experiments probing vibrational dephasing, the beam $\omega_1$ was split in two for CARS; one was used as the pump beam and the other underwent a variable time delay to be used as the probe beam.

Vibrational resonance enhancement of the four wave mixing signal appears to be at least two orders of magnitude. The observed line shape is asymmetric. From the analysis of the line shape we do not find any evidence of a strong two-photon contribution to $\chi^{(3)}$. The observed vibrational dephasing in the time-resolved study is very fast at both room temperatures and 4 K, being within the time resolution available. From the combined analysis of the frequency domain and time-resolved studies at both room
temperature and 4 K, an inhomogeneous mechanism of dephasing is inferred. This inhomogeneous dephasing arises from simultaneous coherent excitation of a distribution of polymer conjugation length. This work is published\textsuperscript{5}.

Several types of studies were performed with Langmuir-Blodgett films. Most studies focused on various diacetylene polymers. Diacetylens have received considerable attention because of their ability to form highly ordered polymers by topochemical polymerization in the solid state. The polydiacetylens are highly conjugated linear polymers which exhibit anisotropic optical properties as well as strong third-order nonlinear interaction. Potential applications of polydiacetylene are ultrathin resins, protective coating, or as integrated optical devices.

Coherent thin films of poly bis(p-toluene sulfonate) diacetylene were successfully formed by modified Langmuir-Blodgett techniques using two methods: (1) photopolymerization of the monomer film at the gas/liquid interface and then transfer to a solid substrate and (ii) transfer of the monomer film to the solid substrate with subsequent photopolymerization on the substrate itself. The films thus obtained were characterized by traditional force-area isotherms while on pure water subphase. Segments were transferred at either 1 dyne/cm or 10 dyne/cm surface pressure, in different stages of photopolymerization, to glass or germanium substrates. The films on the substrates were characterized by the methods of multiple attenuated internal reflection infrared spectroscopy, ellipsometry, contact potential measurement, and Laser Raman spectroscopy. Our results show that the films are multimolecular and about 100 Å thick. Of special interest was the observation of significant anisotropy of oriented dipoles, and the ability to obtain excellent spectral data for these very thin oriented films. Raman spectroscopic features are similar to those observed for the
bulk polymer, even in the low frequency region. Polarized Raman spectroscopy confirmed the presence of local anisotropy in these films. This work has been published \(^6\).

One special group of diacetylene has the general formula

\[
C_{m+1}H_{2m+1} - C\text{-}C\text{-}(\text{CH}_2)_n\text{-COOH.}
\]

These amphiphilic diacetylenes form traditional mono and multilayer Langmuir-Blodgett (from here on abbreviated as L-B) films. Photopolymerizations have been observed in these L-B films to produce highly oriented polymer films. It has been reported that the polymers formed in the L-B films are initially in a blue (non-fluorescing form) but subsequently transform to a red form which is highly fluorescent. The exact nature of this transformation is not established, although it is agreed that the \(\pi\)-electron conjugation in the red form is reduced.

We conducted the structural studies of mono and multilayer L-B films of a specific polydiacetylene with \(m=12\) and \(n=8\) by using the technique of Raman optical wave guide. The Raman optical wave guide technique has successfully been used in the vibrational study of many polymer films. The technique does not rely on any specific enhancement from the surface of the substrate such as in the case when the film is deposited on silver. In addition, the study of polydiacetylene films in an optical wave guide system is also of interest from the point of view of its application in integrated optical devices. These films were deposited on several different kinds of optical wave guide to examine the effect of the substrate.

Coherent mono and multilayer films of poly 11-8 diacetylenic fatty acid were formed by the L-B technique. The films thus formed were characterized by traditional force-area isotherms while on pure water subphase. Molecular organization in both mono and multilayer films was investigated by the
resonance Raman optical wave guide method. Our results show that the molecular organizations in both the monolayer and multilayer films are the same and also show no dependence on the nature of the substrate. Furthermore, both monolayer and multilayer films can be prepared in either blue or red forms. The study of the Raman spectral change as a function of the blue-to-red polymer form conversion reveals that the phase transformation involves a two-phase heterogeneous process. This work is published.

Another exciting result of our L-B film research is our recent discovery that in poly-4-BCMU, the ultrastructure of the polymer film can be controlled by varying the surface pressure. A solution of poly-4-BCMU in toluene was spread over a water subphase in a Langmuir trough. The monolayer film was compressed and the surface pressure was measured by the Wilhelmy balance. The isotherm at each temperature reveals a plateau indicating a phase transition. The monolayer film transferred on a glass substrate at low surface pressure is yellow which in solution has been characterized to involve a coil structure. This is the first time a yellow condensed form has been prepared, because films cast from solvent evaporation are always found to have rod polymer conformation of the red form. As the surface pressure is increased the film turns to the red form, the plateau indicating a first-order transition. To our knowledge, this is the first evidence of a surface pressure induced conformational change (coil-to-rod) in a synthetic polymeric system. This work is published.

A novel application of the quartz crystal microbalance was demonstrated in a study of L-B films. An oscillating quartz crystal can be used as a very sensitive mass measuring device because its resonance frequency changes upon the deposition of a given mass to the crystal surface. The application
of this phenomenon is wide-spread and has led to the terming of this use of a quartz crystal as the quartz crystal microbalance. Sensitivities on the order of 1 nanogram are readily obtained, and the change in frequency is a linear function of the mass attached to the surface of the crystal. The sensitivity of the quartz crystal microbalance makes it ideally suited to study fractional monolayer and multilayer films. Knowledge of the mass deposited can provide useful information about molecular organization in such films.

We reported our initial results applying the quartz crystal microbalance technique to study calcium stearate monolayer and successively deposited multilayer L-B films. The quartz crystal microbalance was found to have the sensitivity and reproducibility necessary to determine the mass of material associated with the deposition of L-B monolayer thick films. In the case of calcium stearate films deposited on gold, we found a linear relationship between the change in mass attached to a quartz oscillator crystal and the number of layers deposited. Our experimental results suggest that some water may be incorporated between layers of multilayer thick films and/or the substrate's surface topography may create a slightly larger effective area for film formation. This work is published⁹.

Third harmonic generation was observed for the first time from a monolayer film on water subphase. This study, conducted for a polydiacetylene, poly-4-BCMU, reveals a conformational transition in the monolayer film whereby the effective π-electron conjugation is reduced. From the study, the orientation of the polymer at the water subphase and the value of the second hyperpolarizability, \( \gamma \), along the polymer chain was determined. The corresponding bulk susceptibility, \( \chi^{(3)} \) was found to be in agreement with those reported by earlier studies. This work is published¹⁰.
Electrochemically formed homo-polyazulene and mixed polyazulene-polypyrrole films were studied by infrared spectroscopy. Infrared spectra are consistent with a polymerization mechanism that involves loss of hydrogen atoms and produces an amorphous polymer structure. The spectral differences between the oxidized (conducting) and reduced (nonconducting) forms of polyazulene show the presence of a polarization interaction in the oxidized polymer, even though the structure of both forms is similar. The i.r. bands of anions are present only for the oxidized form of the polymer, a result that indicates the existence of cationic charge centers on the polymer backbone. The counter anions have no detectable effect on the polymer structure and only a small effect on certain vibrational bands of the oxidized form. The electrochemical preparation of a mixed polyazulene-polypyrrole phase is discussed and the mixed phase is found by i.r. spectroscopy to be a random copolymer. A bilayer polymer structure consisting of polyazulene and polypyrrole was also prepared and the i.r. spectra of this polymer structure did not indicate any interfacial interactions. This work is published.\(^\text{11}\)

Another interfacial method used to produce thin polymer films involved reactions at the solid-gas interface. The reaction at solid-gas interface involved the use of a thin monomeric film, vacuum deposited, which was subsequently exposed to a strong Lewis acid such as \(\text{AsF}_5\) in a controlled atmosphere. We produced two new polymers using this method; these are polyfuril and polyazulene. When furil, a bright yellow compound rich in conjugated \(\pi\)-electrons, was exposed to \(\text{AsF}_5\) for 24 hours, it turned dark blue with a metallic luster. Elemental analysis showed results consistent with a 6-7 unit polymer formation by hydrogen abstraction. The polymer was found to be stable up to 500°C. Prolonged heating at this temperature
appears to produce a more rigid new structure. IR spectra of the reactant and the product exhibit differences, again, consistent with polymerization. X-ray powder diffraction studies conducted on both the polymer and the monomer reveal that the polymer produced is also crystalline and forms a lattice similar to that of the monomer. The work on polymerization of furil has been published. For the structural characterization and the dynamics of electron transport, a highly suitable method is that of inelastic electron tunneling spectroscopy (IETS). In the inelastic electron tunneling spectroscopy, one measures the tunneling current (I) vs the applied voltage (v) across a junction metal-insulator-metal. If the junction has energy states like vibrational states and phonon states which can scatter the tunneling electrons, inelastic tunneling occurs. In such a case, the second derivative \( \frac{d^2I}{dv^2} \) when plotted against the voltage v contains features which relate to the scattering states. Therefore, one can obtain information about the vibrational (or phonon) states of the metal or the insulator forming the junction. This provides an excellent method of obtaining vibrational spectra of ultra submicron polymeric films which can be used to fabricate the junction. Since there is no optical selection rule, all vibrational bands can appear in the IETS spectra. In order to obtain the \( \frac{d^2I}{dv^2} \) vs v curve, one has to build an inelastic electron tunneling spectrometer, since such a device is commercially not available. We have successfully built and tested this spectrometer with benzoic acid as the reference material. We have completed study of the Langmuir-Blodgett films of the 4-BCMU diacetylene monomer and polymer. Our results suggest that the
red form of poly-4-BCMU, when transferred on the aluminum oxide, undergoes a conformational transition to a more flexible, yellow form.

We have also studied a family of aromatic diketones (furil, piridil, benzil). Results of this work suggest that diketones interact strongly with alumina and are chemisorbed in the enolic form. This work was reported at the ACS meeting in Denver.\textsuperscript{13}

Chemical doping of polymers is a highly active field of research because the chemical doping has been successfully used to increase the electrical conductivities of several polymers as well as to induce conformational changes in some polymers. It has been suggested that when an amorphous film of an oriented \( \alpha \)-rich film of nylon-6 is treated with iodine, the development of an oriented Y-form takes place. We investigated the nature of the iodine-nylon 6 complex by resonance Raman spectroscopy. This work reveals the presence of both \( I_3^- \) and \( I_5^- \) species, the latter most likely in the form of an \( I_2/I_3^- \) complex. Polarization characteristics of the Raman Spectra show that these two types of species are oriented differently. The \( I_2/I_3^- \) ions were suggested to be perpendicular to it. The \( I_2/I_3^- \) units were found to be in a more stable moiety than the \( I_3^- \) species. A correlation of the Raman results with those of X-ray diffraction was found to be satisfactory. A paper on this work has been published.\textsuperscript{14}
PUBLICATIONS RESULTING FROM AFSR SUPPORT
(Also serves as references for the Progress Report)


OTHER PUBLICATIONS


INVITED TALKS


5. State University of New York at Stony Brook, Department of Chemistry, April 10, 1986.
   "Design, Ultrastructure and Dynamics of Non-linear Optical Effects in Polymeric Thin Films".

   "Dynamics of Solid State Polymerization".

   "Design, Ultrastructure and Dynamics of Non-linear Optical Interaction in Polymeric Thin Films".

   Non-linear Optical Interactions in Polymer Thin Films".

   "Nonlinear Optical Effects in Organic Polymeric Films -- Can Optical Computers Work!"

    "Reactions Involving Laser Driven Plasma".

    "Nonlinear Optics of Ordered Polymers"

12. Standard Oil of Ohio, Cleveland, November 8, 1986
    "Design, Ultrastructure, and Dynamics of Nonlinear Optical Interactions in Polymeric Films".

    "Picosecond and Subpicosecond Four Wave Mixing Study of Dynamics of Energy States".

    "Design, Ultrastructure and Dynamics of Nonlinear Optical Effects in Polymeric Films".

    "Organic Nonlinear Optics".

    "Nonlinear Optical Effects in Organic Polymeric Films"

    "Nonlinear Optical Effects in Thin Polymeric Films".
18. Wright-Patterson Air Force, Polymer Branch, Dayton, Ohio, March 9, 10, two day Tutorial on Organic Nonlinear Optics.


A. Post-doctoral Fellows
   1. Dr. J. Swiatkiewicz
   2. Dr. R. Burzynski
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   4. Dr. B. P. Singh

B. Graduate Students
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D. Secretary
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