Photonic and Opto-Electronic Applications of Polydiacetylene Films Photodeposited from Solution and Polydiacetylene Copolymer Networks

Mark S. Paley,[a] Donald O. Frazier,[b] David D. Smith,[b] William K. Witherow,[b] Hossin A. Abdeldeyem,[a] and Daniel B. Wolfe[c]

[a]Universities Space Research Association, Huntsville, AL
[b]Marshall Space Flight Center, Huntsville, AL
[c]Rice University

ABSTRACT

Polydiacetylenes (PDAs) are attractive materials for both electronic and photonic applications because of their highly conjugated electronic structures. They have been investigated for applications as both one-dimensional (linear chain) conductors and nonlinear optical (NLO) materials. One of the chief limitations to the use of PDAs has been the inability to readily process them into useful forms such as films and fibers. In our laboratory we have developed a novel process for obtaining amorphous films of a PDA derived from 2-methyl-4-nitroaniline using photodeposition with UV light from monomer solutions onto transparent substrates. Photodeposition from solution provides a simple technique for obtaining PDA films in any desired pattern with good optical quality. This techique has been used to produce PDA films that show potential for optical applications such as holographic memory storage and optical limiting, as well as third-order NLO applications such as all-optical refractive index modulation, phase modulation and switching. Additionally, copolymerization of diacetylenes with other monomers such as methacrylates provides a means to obtain materials with good processibility. Such copolymers can be spin cast to form films, or drawn by either melt or solution extrusion into fibers. These films or fibers can then be irradiated with UV to photopolymerize the diacetylene units to form a highly stable cross-linked PDA-copolymer network. If such films are electrically poled while being irradiated, they can achieve the asymmetry necessary for second-order NLO applications such as electro-optic switching. On Earth, formation of PDAs by the above mentioned techniques suffers from defects and inhomogeneities caused by convective flows that can arise during processing. By studying the formation of these materials in the reduced-convection, diffusion-controlled environment of space we hope to better understand the factors that affect their processing, and thereby, their nature and properties. Ultimately it may even be feasible to conduct space processing of PDAs for technological applications.

1. INTRODUCTION AND BACKGROUND

Polydiacetylenes (see structure below) are a class of highly conjugated organic polymers that are of considerable interest because of their unique chemical optical and electronic properties.[1-3] They have been investigated extensively as nonlinear optical materials, as well as potential organic conductors and semi-conductors. PDAs are among the best known third-order NLO materials with $\chi^{(3)}$ values that can be as large as 10^{-9} esu.[4] One of the primary limitations to the use of PDAs for applications has been the difficulty in processing them into useful forms such as thin films and fibers. The standard techniques for obtaining PDA films have involved the growth of crystalline or Langmuir-Blodgett diacetylene monomer films, followed by topochemical polymerization of these monomer films in the solid state. However the growth of suitable quality monomer films can be very tedious and difficult, and furthermore, not all monomer films polymerize readily in the solid state to yield PDA films.[5]

$$\begin{array}{c} \diagdown \\ \diagup C - C \equiv C - C \diagup \\ X \end{array} \begin{array}{c} Y \\ \diagup \\ \diagdown \end{array}$$
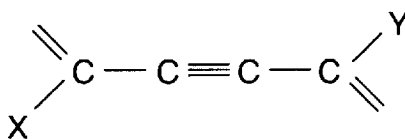
STRUCTURE OF POLYDIACETYLENE REPEAT UNIT

In our laboratory a novel process has been developed for the formation of thin amorphous films of a PDA derived from 2-methyl-4-nitroaniline (MNA), a well-known organic NLO material.[6,7] This process consists of photodeposition of polymer films directly from monomer solutions by irradiation with UV light through a transparent substrate such as quartz or glass (US patent #5,451,433). The resulting PDAMNA films have good optical transparency in the near infrared and exhibit reasonable third-order NLO susceptibilities. Such films have potential for photonic applications such as all-optical refractive index modulation and switching, as well as holographic memory storage and optical limiting. Photodeposition of PDAMNA films is simple and straightforward, and can be used to produce films in desired patterns for possible devices such as waveguides. Once formed, however, the PDAMNA films are quite intractible; they cannot be processed any further. To overcome this limitation, we have been investigating the use of blends and copolymers of PDAs with other materials that do have good processibility. One class of optical polymers that are readily processible is methacrylates; thus we are studying blends of PDAMNA with poly(methyl methacrylate), as well as copolymers of PDAMNA with methacrylates, in order to obtain materials with good processibility. These materials can be spin cast into films, and then can be electrically poled to induce assymetry, which opens up the possibility of second-order NLO applications such as second-harmonic generation or electro-optic switching. If the material is then cross-linked to form a polymer network, systems with good thermal stability and temporal stability against relaxation should be achievable. Addionally these materials are amenable to processes such as melt or solution extrusion, and thus could possibly be formed into nonlinear optical fibers.

The purpose of this article is to elaborate upon the work described above, much of which is currently in progress. Results that have been obtained will be discussed, as well as planned research and potential applications. Lastly, we will briefly discuss the effects of Earth's gravity on the processing, nature and properties of these materials, and how they might benefit from processing in the reduced-convection, diffusion-controlled environment of microgravity.

2. PHOTODEPOSITION OF PDAMNA FILMS FROM SOLUTION

The process of growing a PDA film using photodeposition from solution is very simple and straightforward: a dilute solution of the diacetylene monomer (DAMNA, structure below) is irradiated through a transparent substrate with UV light and a PDAMNA film is deposited on the substrate surface in contact with the solution.

$$HOCH_2 - C \equiv C - C \equiv C - CH_2 - NH - \underset{}{\underset{}{\bigcirc}} - NO_2$$
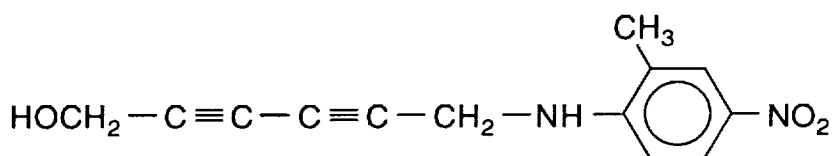
DAMNA

The quality and thickness of the film depend on the solvent, monomer concentration, and the wavelength and intensity of the UV light; in the case of PDAMNA the best films are obtained using a DAMNA concentration on the order of 10^{-2} moles/liter in 1,2-dichloroethane, and it takes about a day to grow a film with thickness 0.5 - 1.0 μm using 366nm light with intensity of a few mW/cm^2. A variety of substrates can be used as long as they are UV transparent; thus far PDAMNA films have been grown on quartz, glass, indium-tin oxide coated glass, sodium chloride, polyethylene terephthalate, and other surfaces. Masking experiments have demonstrated that film deposition occurs only where the UV light comes directly in contact with the substrate, indicating that the process is occurring at the surface.

SUBSTRATE

MONOMER
SOLUTION →

UV

THIN FILM
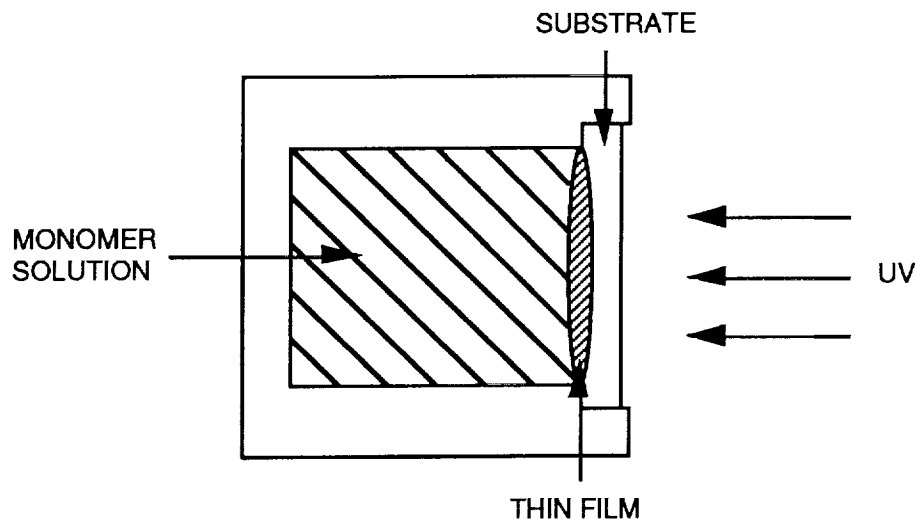
PDAMNA films grown onto quartz substrates have a glassy yellow-orange appearance; electron diffraction studies and refractive index measurements indicate that the films are essentially amorphous. They are transparent in the near-infrared down to about 750nm, and then exhibit increasing absorption at shorter wavelengths. PDAMNA films are insoluble in common organic solvents such as benzene, acetone, alcohol, dimethyl sulfoxide, etc., although some of these solvents can cause them to peel off of the substrate.

3. THIRD-ORDER NLO PROPERTIES OF PDAMNA

The optical quality of PDAMNA films photodeposited from solution is reasonably good (however, see section 8), and the films obtained are capable of waveguiding. Linear refractive index measurements obtained from normal mode analysis using a prism coupler at 632nm (in the tail of the absorption band) give a value of about 1.70. When measured at 810nm (a nonresonant wavelength), this value drops only slightly to about 1.68.[8] At neither of these wavelengths do the films exhibit any significant birefringence.

Degenerate 4-wave mixing (DFWM) experiments carried out at 532nm on PDAMNA films (thicknesses around 1.0μm) using a Nd-Yag laser with nanosecond pulses yield $\chi^{(3)}$ values on the order of 10^{-8} to 10^{-7} esu. Because 532nm is in the absorption edge of the polymer, the values obtained are resonance enhanced. Typically, $\chi^{(3)}$ values for polydiacetylenes can vary by several orders of magnitude depending on the degree of resonance enhancement and other factors.[9,10] The largest reported non-resonant (purely electronic) $\chi^{(3)}$ value for a polydiacetylene is on the order of 10^{-9} - 10^{-10} esu for PTS single crystals.[4] Preliminary DFWM measurements carried out on the PDAMNA films at 810nm using 125 femtosecond pulses from a Ti-Sapphire laser give $\chi^{(3)}$ values on the order of 10^{-11} - 10^{-12} esu.[8] There was no observable slow decaying tail and no detectable two-photon absorption, therefore at this wavelength the nonlinearity is non-resonant electronic. Although the magnitude of the non-resonant third-order nonlinearity of the PDAMNA films is not outstanding, and is considerably less than for PTS crystals, it is comparable to or better than other conjugated organic

polymers, including other PDAs. Furthermore, the nonlinearity of the PDAMNA films has by no means been optimized; the films are amorphous and thus the polymer chains are not aligned as in a crystal (e.g. PTS), nor has the chemical structure been modified to maximize the inherent nonlinearity. Work in these areas is underway, some of which will be discussed later. Lastly, to ascertain the true potential for device applications (the figures of merit), thorough measurements of light scattering, linear absorption, two and three-photon absorption, damage thresholds, etc. must be carried out.[11]

4. WAVEGUIDE DEVICES AND HOLOGRAPHIC MEMORY STORAGE

The fact that photodeposition of PDAMNA films from solution occurs only where the substrate is directly exposed to UV light can be exploited to produce films in desired patterns for potential devices. For example, if the growth cell is mounted on a computer controlled x-y translation stage and a UV laser is focused on the substrate, a complex waveguide pattern can be formed quite easily. In order to produce a viable waveguide device, the optical setup must be optimized in order to give sharp lines with good optical quality.

Another very promising application of photodeposition of PDAMNA films is holographic information storage. Holograms can made readily from PDAMNA using a standard sideband holographic setup, as has been demonstrated in our laboratory. The laser source was an argon ion laser with a wavelength of 365 nm. A beamsplitter split the output beam into a reference beam and an object beam. The object was a transparent plastic with the letters NASA printed on it. The two beams were incident on a test cell containing a quartz window and the DAMNA monomer solution. Interference took place at the quartz window/solution interface to create the complex diffraction grating that makes up a hologram, and PDAMNA was deposited on the quartz window to record the hologram.

A helium-neon laser with a wavelength of 632.8 nm was then used to reconstruct the PDAMNA holograms. The reconstructed hologram reproduced the object wavefront, recreating the NASA lettering. Because photodeposition is not reversible, the holograms produced are permanent.

5. MOLECULAR ENGINEERING OF PDAMNA

As stated earlier, the third-order NLO susceptibility of the PDAMNA films is on the order of 10^{-11} esu, which is reasonable but not outstanding. In order to be efficient for photonic applications, this quantity needs to be maximized. One of the advantages of organic and polymeric NLO materials over inorganic and semiconductor materials is the ability to tailor the material to meet specific needs by altering the molecular structure. Such molecular engineering allows great design flexibility with a wide range of structural possiblities. Research into optimizing the $\chi^{(3)}$ value of PDAMNA is currently underway.

One approach to enhancing $\chi^{(3)}$ is to improve the alignment of the polymer chains in the PDAMNA films, thereby allowing the NLO-active moieties (the conjugated backbones) to all respond in the same direction. Both AFM and SEM data taken on PDAMNA films show that the polymer chains show a very weak tendancy to align in the direction normal to the substrate surface. We are attempting to improve this alignment by incorporating liquid crystalline groups into the structure.[12] One promising compound that has just been synthesized is the following:
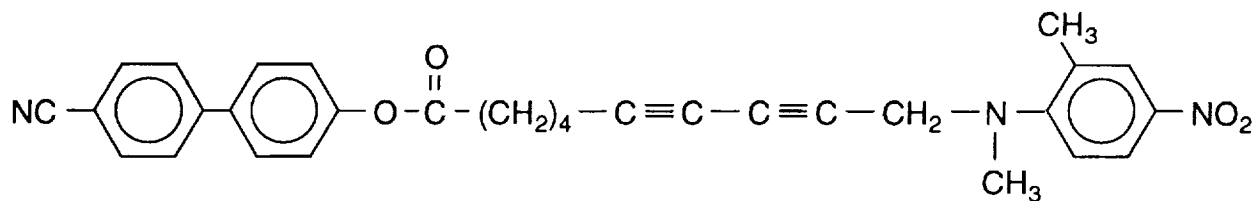
Analysis by differential scanning calorimetry indicates that this diacetylene monomer does appear to exhibit liquid crystalline behavior. The next task is to grow a PDA film from this monomer and determine if indeed the polymer chains are well-aligned.

Another approach to improving the third-order nonlinearity of the PDAMNA films is to modify the structure with groups that will increase the inherent nonlinearity of the molecule itself. One way to achieve this is to use cross-conjugated side groups; i.e., use side groups that are in conjugation with the polymer backbone. Semi-empirical molecular orbital calculations have demonstated that the γ values (the molecular analog of $\chi^{(3)}$) for cross-conjugated PDAs are generally larger than for non-cross conjugated PDAs. Thus we expect that the following cross-conjugated analog of PDAMNA will have a larger $\chi^{(3)}$ than PDAMNA itself:

$$\text{HOCH}_2-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CH}=\text{NH} - \overset{\text{CH}_3}{\underset{}{\bigcirc}} - \text{NO}_2$$
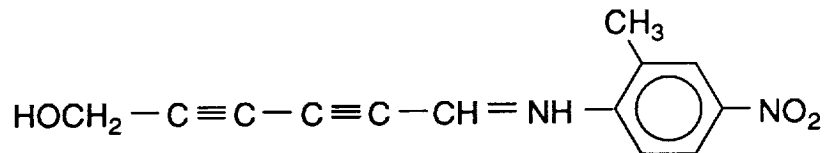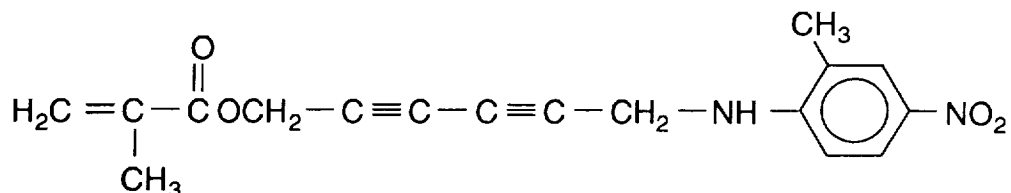
Experiments are forthcoming in this area.

6. BLENDS AND COPOLYMERS OF PDAMNA WITH OTHER MATERIALS

As we have discussed photodeposition from solution provides a very convenient means of obtaining PDA films for a variety of potential applications. However, once formed PDAMNA films (and for that matter, most PDAs) are quite intractible materials; they are rigid, brittle, cannot be melted without decomposing, and are quite insoluble. In order to develop materials that can be more readily processible, we have begun investigating blends (mixtures) and copolymers of PDAs with other materials. One class of polymers that offer excellent optical transparency and are easily processible are polymethacrylates such as poly(methy methacrylate), PMMA, i.e., plexiglass. Currently we are synthesizing, characterizing and preparing films of both blends and copolymers of PDAMNA with PMMA.

The preparation of blends of PDAMNA with PMMA is quite straightforward. A solution containing PMMA and DAMNA is prepared in some organic solvent that is suitable for spin coating. Films are then spin cast, and the solvent is evaporated leaving a PMMA film containing dissolved DAMNA. Upon irradiation with UV light, the DAMNA monomer units can polymerize to form PDAMNA within the PMMA matrix. The degree of polymerization is a function of the concentration of DAMNA, the intensity of the light, and the mobility of the DAMNA molecules inside the PMMA (which appears to be surprisingly high at room temperature). If this system is electrically poled during irradiation, the DAMNA molecules can be aligned (in particular, the MNA portion which has a large dipole moment) as they polymerize. This should yield a material that not only would have enhanced third-order nonlinearity, but that would also possess the necessary asymmetry for second-order NLO effects. The inherent second-order nonlinearity of the MNA, possibly enchanced by the polydiacetylene, could provide a useful material for applications such as electro-optic swithcing. As stated earlier, this work is just underway and results will be forthcoming.

One drawback of poled polymer blends is the problem of thermal relaxation; i.e., when the electric field is removed the aligned molecules slowly return back to a random orientation. In order to get around this problem scientists have turned to cross-linked polymer systems and copolymer networks to increase rigidity by essentially locking the molecules into place. Hence we are investigating the potential of a copolymer network formed from a polymethacrylate derivative of PDAMNA. We have synthesized the following monomer:

$$H_2C = C - \overset{\overset{\displaystyle O}{\|}}{C}\, OCH_2 - C \equiv C - C \equiv C - CH_2 - NH - \langle\!\!\bigcirc\!\!\rangle - NO_2$$
$$\underset{CH_3}{|}$$

(benzene ring bears a CH_3 substituent; NO_2 para)

This monomer contains both diacetylene and methacrylate groups, both of which are polymerizable independently. If only the methacrylate groups are polymerized, the resulting polymer will be a polymethacrylate containing diacetylene side groups. This polymer may have good processiblility itself, but, if not, a copolymer from this monomer and methyl methacrylate should be readily processible; previous work on other methacrylate/NLO dye systems has shown that homopolymers are often difficult to work with, but copolymers are not.[13] Films can then be spin cast from the DAMNA-polymethacrylate polymer, poled, and then irradiated during poling to now polymerize the diacetylene groups, yielding a cross-linked PDAMNA/polymethacrylate copolymer network. Such a system would have very high rigidity and thus should be very resistant to relaxation.

Lastly, we want to briefly mention one other promising use for PDAMNA blends and copolymers besides thin films, namely, NLO fibers. Because these DAMNA-polymethacrylate based materials are soluble in organic solvents, and in some cases can be melted without decomposition, they are readily amenable to being drawn into fibers by either melt or solution extrusion techniques. Fiber optics are playing an increasingly important role in the telecomunnications industry, and the ability to readily produce a high quality optical fiber that has good NLO properties would be of great value.

7. MICROGRAVITY RELEVANCE

One factor that is often tacitly ignored in the processing of materials is the influence of Earth's gravity, primarily via effects such as natural convection and sedimentation. It is well-known, however, that these effects, especially convection, can affect heat and mass transport processes in solution.[14] Photodeposition of polydiacetylene films from solution is no exception. We shall first discuss how buoyancy-driven convection can arise during photo-deposition of PDAMNA films from solution, and then describe how this convection can effect the morphology, microstructure, and properties of the films obtained.

Both the monomer solution and the film generate heat due to absorption of UV radiation. The radiative heating, along with the thermal boundary conditions of the walls of the thin film growth chamber, will give rise to a complex temperature pattern in the solution. Due to the lack of thermodynamic equilibrium, the solution will possess thermal density gradients. Density gradients can also arise in the solution due to variations in the concentrations of the chemical species present in the solution. These gradients, under the influence of gravity, can induce convective fluid flows in the solution (buoyancy-driven convection). The extent of convection, and its intensity and structure can only be understood through accurate numerical modeling of the fluid motion and thermodynamic state of the system. Preliminary simulations of the fluid flow have been conducted.[15]

One significant effect of convection can be seen when PDAMNA films grown in 1-g are viewed under an optical microscope: they exhibit small particles of solid polymer embedded throughout. These form when polymer chains in the bulk solution collide due to convection and coalesce into small solid particles, on the order of 0.01 - 1.0 micron in size. Because these particles are very small, almost colloidal in nature, they do not sediment out readily, and thus remain suspended in the bulk solution. Convection then transports these particles to the surface of the growing film where they become embedded. These particles are defects that can scatter light and thus lower the optical quality of the films.

To study the effects of convection on the formation of particles in the films, the growth chamber was placed in different orientations with respect to gravity in order to vary the fluid flow pattern. PDAMNA films were grown with the chamber vertical (irradiating from the top), which is the least convective configuration, and with the chamber horizontal (irradiating from the side), which has more pronounced convection. Films grown with the chamber horizontal clearly contained a greater concentration of particles than films grown with the chamber vertical. This is consistent with expectations based on the relative amounts of convection in the two orientations; films grown under increased convection contain more particles than those grown under less convection. Also, waveguiding experiments with these films demonstrate that the films containing more particles exhibit greater light scattering than those containing fewer particles.

In Sept. 1995 we conducted an experiment aboard the Space Shuttle Endeavor (CONCAP-IV) in which photodeposition of PDAMNA films from solution was carried out in microgravity. In this environment buoyancy-driven convection can essentially be eliminated. Because of unplanned orbiter maneuvers during the mission, leading to extraneous accelerations, and limitations of the flight hardware, results varied somewhat among samples. However, the best space-grown film clearly exhibited fewer particles than the best ground-based films. These few particles may have resulted from slight mixing in the solution caused by the orbiter motions, or possibly, they may have nucleated on the surface the film itself. Nonetheless, the initial results are very encouraging; it appears that the lack of convection can indeed lead to PDAMNA films with significantly fewer defects, and thus greater optical quality. Further characterizations of the space-grown films are currently underway.

Finally, it should be mentioned that convection can affect PDAMNA film growth in other ways. The growth kinetics of the film are influenced by fluid flows, as are the morphology and microstructure (e.g., polymer chain alignment). These effects are manifested in the nature and properties of the film, including the NLO properties. Also, gravity induced flows can occur in the PDAMNA-polymethacrylate systems, despite the fact that they are quite viscous because they are polymeric. Optical fibers drawn from these materials could suffer because non-newtonian flows that arise during processing can cause inhomogeneities and defects that may lead to optical signal losses.

8. CONCLUSIONS

In summary, we have presented an overview of the techniques and potential applications of photodeposition of PDAMNA films from solution and PDAMNA blends and copolymer systems. These materials are relatively easy to handle and show good potential for a wide variety of applications including all-optical information processing, holographic memory storage, electro-optic switching, and NLO fibers. Lastly, we believe that studies on the effects of gravity, primarily buoyancy-driven convection, should be a part of any research into the processing of PDAMNA for photonic and electro-optic materials. Results obtained from such studies can then be used to optimize processing conditions on the ground; also, someday processing in space may become technologically feasible (e.g. aboard the Space Station).

9. ACKNOWLEDGEMENTS

10. REFERENCES

1. *Polydiacetylenes*, Bloor, D.; Chance, R. R. Eds.; Martinus Nijhoff Publishers: Dordrecht, The Netherlands, **1985**.

2. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Vol. 2, Chemla, D. S.; Zyss, J. Eds.; Academic Press: Orlando, FL, **1987**.

3. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Prasad, P. N.; Williams, D. J.; John Wiley and Sons, Inc., New York, **1991**.

4. Reference 2, Vol.2, Chapter III-3.

5. Thakur, M; Meyler, S. *Macromolecules* **1985**, *18*, 2341.

6. Paley, M. S.; Frazier, D. O.; Abdeldeyem, H.; Armstrong, S.; McManus, S. P.; *J. Am Chem. Soc.* **1995**, *117(17)*, 4775.

7. Paley, M. S.; Frazier, D. O.; McManus, S. P.; Zutaut, S. E.; Sangahadasa, M. *Chem. Mater.* **1993**, *5(11)*, 1641.

8. Samoc', M.; Australian National Laboratory Laser Physics Centre; personal communication.

9. Reference 3, p.232-233.

10. Etemad, S.; Baker, G. L.; Soos, Z. G. in *Molecular Nonlinear Optics*; Zyss J., Ed., Academic Press: San Diego, CA, 1993.

11. Stegeman, G. I.; Torruellas, W. in *Electrical, Optical, and Magnetic Properties of Organic Solid-State Materials*; Garito, A. F.; Jen, A. K.-Y.; Lee, C. Y.-C., Dalton, L., Eds.; MRS Symposium Proceedings; Materials Research Society: Pittsburg, PA, 1994; p. 397-412.

12. Wolfe, D. B.; Paley, M. S.; Frazier, D. O., manuscript in preparation.

13. Müller, H.; Nuyken O.; Strohriegl, P., *Makromol. Chem., Rapid Commun.* **1992**, 125.

14. *Fundamentals of Low-Gravity Fluid Dynamics and Heat Transfer*, Antar, B. N.; Nuotio-Antar, V. S., CRC Press, **1994**.

15. Frazier, D. O.; Hung, R. J.; Paley, M. S.; Long, Y. T., *J. Cryst. Growth* **1997**, 172.