Photodeposition of Thin Polydiacetylene Films from Solution That Exhibit Large Third-Order Optical Nonlinearities

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One promising class of organic compounds for applications in the field of nonlinear optics (NLO) are polydiacetylenes,[1] which are of interest because they are highly conjugated polymers capable of exhibiting very large optical nonlinearities with fast response times. Their long polymeric chains render polydiacetylenes readily conducive to the formation of thin films, thereby making them useful for devices such as waveguides and integrated optics. Hence they have been studied extensively as NLO materials, in particular, as third-order NLO materials. The typical methods for making polydiacetylene thin films involve growth of thin crystalline films of diacetylene monomers, followed by topochemical polymerization of these films in the solid state to give crystalline polydiacetylene films.[2] However, the growth of high-quality, large-area single-crystalline thin films (by methods such as epitaxy) is not trivial.[3] Unfortunately, no method exists which is generally applicable to the formation of polydiacetylene thin films possessing the high optical quality necessary for device applications. The difficulty in processing these materials readily into usable forms has been one of the chief hindrances to the use of polydiacetylenes (as well as other organic and polymeric materials) for commercial NLO applications.

During the course of crystal growth studies in anticipation of a space experiment, we have discovered a novel, simple method for the formation of polydiacetylene thin films by photodeposition from monomer solutions onto quartz or glass substrates. Specifically, we have synthesized and characterized a diacetylene monomer, DAMNA, that sluggishly polymerizes when the

$$HOCH_2-C\equiv C-C\equiv C-CH_2-NH-\underset{\text{DAMNA}}{\text{(C}_6\text{H}_3\text{)(CH}_3\text{)}}-NO_2$$
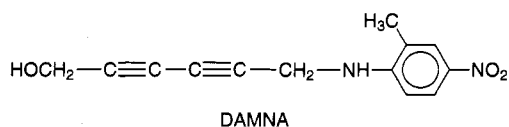
DAMNA

crystalline monomer is irradiated.[4] However, thin polydiacetylene (PDAMNA) films can be obtained readily
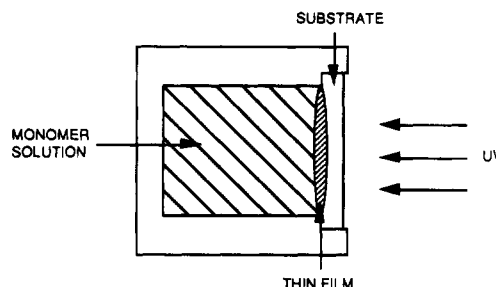

Figure 1. Diagram of the apparatus used for the photodeposition of polydiacetylene thin films from solution.

from dilute solutions (3–4 mg/mL) of DAMNA in 1,2-dichlorethane by irradiation over a 2-day period with long-wavelength (366 nm) UV light from a 15-W lamp through a transparent window, which serves as the substrate (Figure 1). These films possess superior optical quality (i.e., greater homogeneity, fewer defects) than those generally obtained via solid-state polymerization. This is primarily because films obtained by solid-state polymerization are crystalline, whereas those formed by solution-state polymerization are amorphous, evident from the fact that the refractive index is essentially isotropic. Also, electron beam diffraction studies indicate no crystal structure. Hence there are no grain boundaries or other crystal defects that can lower the optical quality and cause light scattering. The PDAMNA films obtained by photodeposition from solution are yellow-orange and have thicknesses between 0.1 and 2.0 μm, which is a useful range for device applications.

Characterization of these PDAMNA films is not trivial; they are not soluble in common organic solvents (even concentrated sulfuric acid does not dissolve the films), which makes the standard solution-based methods of polymer analysis useless. However, ^{13}C NMR spectroscopy was carried out on a DMSO-d_6 solution of PDAMNA precipitated from the bulk solution. Absorptions were observed around 128 and 60 ppm, consistent with the presence of olefinic and acetylenic carbons, respectively.[5]

UV–visible absorption spectroscopy indicates that the PDAMNA films (on quartz substrates) are essentially transparent above 700 nm, then exhibit increasing absorption at shorter wavelengths, with a shoulder peak at 370 nm due to the MNA group, and a maximum between 200 and 300 nm. DAMNA monomer (in 1,2-dichloroethane) is transparent above 450 nm. Thus the red shift in the absorption band is indicative of the polymerization that has occurred. The UV–vis spectrum of PDAMNA films photodeposited from solution matches very well with that of PDAMNA films obtained via solid-state polymerization methods.

One important question is the structure of the polymer. It is well-known that in the solid-state diacetylenes undergo 1,4 polymerization forming linear polymer chains; however, in solution, there exists the additional possibility of 1,2 polymerization, as well as the formation of branched polymers. The FTIR spectrum of a PDAMNA film grown onto KBr shows no absorption in the region from 2000 to 2100 cm^{-1}, which is where

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

(2) Wegner, G. *Z. Naturforsch.* **1969**, *246*, 824. Also: *Solid State Polymerization*; Sandman, D. J., Ed.; American Chemical Society: Washington, DC, 1987.

(3) Thakur, M.; Meyler, S. *Macromolecules* **1985**, *18*, 2341.

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

(5) Schaefer, J.; Sefcik, M. D.; Stejskal, E. O.; McKay, R. A.; Hall, P. L. *Macromolecules* **1981**, *14*, 557.
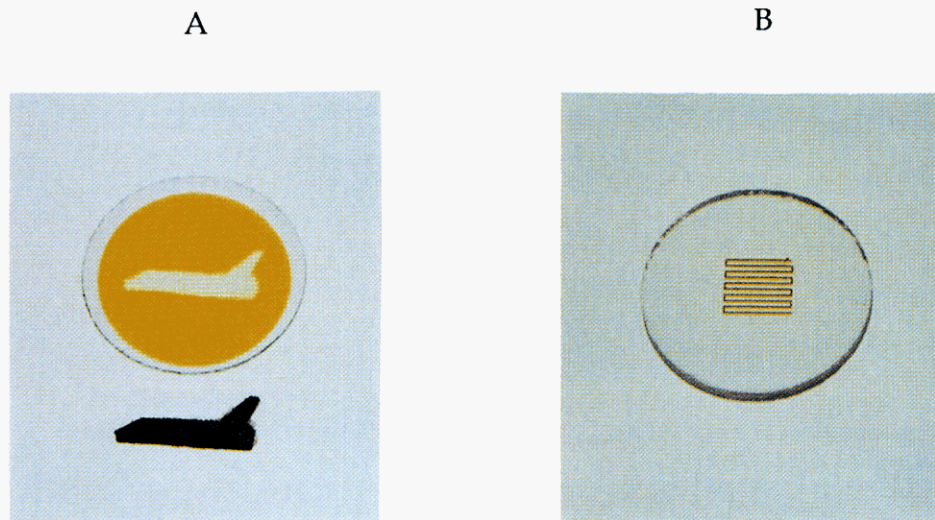
A

B

Figure 2. (A) This PDAMNA film was formed by photodeposition from solution onto a thin glass substrate. A portion of the substrate was blocked from exposure to the UV light by the mask (shown below the film), which was placed on the *opposite* side of the glass disk as the film, clearly demonstrating that photodeposition occurs only where the substrate is irradiated directly. (B) This PDAMNA circuit was photodeposited onto quartz using the UV radiation from an argon-ion laser, a technique which could provide a novel means for producing optical circuits.

carbon−carbon triple-bond vibrations are usually observed. Typically, the backbone vibrations of polydiacetylenes are not IR active because of symmetry considerations; however, side groups do generally show up.[6] Hence, in the case of 1,4 polymerization, because the only carbon−carbon triple bonds present are in the polymer backbone, they are not expected to absorb in the IR. On the other hand, for 1,2 polymerization, the carbon−carbon triple bonds are in the side groups and thus should be expected to absorb in the IR. The absence of carbon−carbon triple-bond absorptions in the FTIR spectrum for PDAMNA would seem to suggest that 1,4 polymerization has occurred. However, at this point, we cannot absolutely rule out that some 1,2 polymerization may also have occurred. The results of these and additional analyses will be discussed in more detail in forthcoming publications.

Because this solution-state photodeposition process is new, all of the parameters controlling the efficacy of thin-film formation are not yet known. We have been carrying out experiments with a variety of diacetylene monomers and have found that their ability to form polymeric thin films in solution is highly structure dependent. Some monomers give little or no thin-film deposition despite undergoing polymerization in the bulk solution; the polymer simply precipitates. The solvent is also a factor; e.g., in 1,2-dichloroethane, transparent PDAMNA films are obtained; in 2-butanone, translucent PDAMNA films are obtained; and in ethanol, no films are obtained. This indicates that thin-film formation depends greatly upon the particular monomer/solvent combination.

The role of the substrate in the photodeposition of these polydiacetylene thin films from solution is also not yet fully understood. A variety of substrates can be used, provided that there is sufficient transparency to UV light; thus far, PDAMNA films have been obtained on glass, quartz, mica, poly(ethylene terephthalate), and KBr. Apparently, direct irradiation at the surface of the substrate is essential for thin film photodeposition

to occur, as is indicated by masking experiments. When a mask is placed in front of the substrate to partially block exposure to the light (the mask is on the exterior surface and is *not* actually in contact with the substrate), the result is that the polydiacetylene film forms only where the substrate is directly irradiated (Figure 2A), even though polymerization takes place throughout the bulk solution. Clearly, this demonstrates that some critical process occurs at the surface of the substrate.

On the basis of the above results, we became interested in the idea of using laser light to carry out photodeposition of PDAMNA, as a possible means of forming optical circuits. Thus we mounted our thin-film growth chamber onto a computer-controlled $X-Y$ translator, which was programmed to trace out a test circuit pattern. The UV radiation from an argon-ion laser was then focused onto the substrate as the translator traced out the desired pattern, yielding a thin PDAMNA optical circuit (Figure 2B). The thickness of the circuit is governed by the intensity of the laser radiation, the translation rate, and the number of times the pattern is traced; and the width of the lines is determined by the width of the laser beam. This novel technique could have potential for applications such as the manufacture of integrated optics.

PDAMNA films formed by photodeposition from solution exhibit good third-order NLO properties. Degenerate four-wave mixing carried out on one such film (approximately 1.0 μm thickness), using a pulsed frequency-doubled Nd:YAG laser at 532 nm and 6 ns pulse duration, revealed a large third-order nonlinear susceptibility ($\chi^{(3)}$) on the order of 10^{-7} esu. This value was obtained at a relatively low laser pump energy of 3.3 mJ. At 604 nm, a $\chi^{(3)}$ value of 10^{-8} esu is obtained. Qualitative measurements indicate that the response time of the polymer is on the order of picoseconds (possibly faster), which is consistent with an electronic mechanism for the nonlinearity. Because 532 and 604 nm are in the absorption edge of the polymer (which becomes transparent above 700 nm), we are currently in the process of obtaining measurements at longer wavelengths to reduce resonance enhancements. The

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(6) In ref 1, Vol. 2, Chapter III-3.

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largest measured nonresonant (purely electronic) $\chi^{(3)}$ value to date is on the order of 10^{-9} esu for thin films of PTS.[7] To ascertain the true device potential of the PDAMNA films, thorough measurements of linear absorption, two-photon absorption, waveguiding, scattering, etc., must be carried out; such experiments are underway and will be the subject of future publications. The excellent phase conjugation and fast response time exhibited by these films could make them candidates for applications such as optical switching and optical communications.

We are currently conducting extensive investigations into the basic science (mechanism, photochemistry, solution, and surface chemistry) governing the polym-

erization of diacetylenes in solution and the photodeposition of polydiacetylene thin films from solution. As stated earlier, characterization experiments are in progress to determine the exact structure of PDAMNA obtained from solution. We shall also thoroughly characterize the NLO properties of the films, including more detailed measurements of $\chi^{(3)}$ values, response times, absorption scattering, and damage thresholds. The simplicity of this photodeposition technique could eventually make feasible the commercial application of polydiacetylene thin films for NLO devices (patent applications are in the works).

(7) Carter, G. M.; Thakur, M. K.; Chen, Y. J.; Hryniewicz, J. V. *Appl. Phys. Lett.* **1985**, *47*, 457. See also ref 1, vol. 2.