Gravitational Effects On the Morphology and Kinetics of Photodepostion of Polydiacetylene Thin Films from Monomer Solutions

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Introduction and Objectives

The goal of this proposed work is to study gravitational effects on the photodeposition of polydiacetylene thin films from monomer solutions onto transparent substrates. Polydiacetylenes have been an extensively studied class of organic polymers because they exhibit many unusual and interesting properties, including electrical conductivity and optical nonlinearity. Their long polymeric chains render polydiacetylenes readily conducive to thin film formation, which is necessary for many applications. These applications require thin polydiacetylene films possessing uniform thicknesses, high purity, minimal inhomogeneities and defects (such as scattering centers), etc. Also, understanding and controlling the microstructure and morphology of the films is important for optimizing their electronic and optical properties. The lack of techniques for processing polydiacetylenes into such films has been the primary limitation to their commercial use.

We have recently discovered a novel method for the formation of polydiacetylene thin films using photo-deposition from monomer solutions onto tranparent substrates with UV light. This technique is very simple to carry out, and can yield films with superior quality to those produced by conventional methods. Furthermore, these films exhibit good third-order properties and are capable of waveguiding. We have been actively studying the chemistry of diacetylene polymerization in solution and the photo-deposition of polydiacetylene thin films from solution.

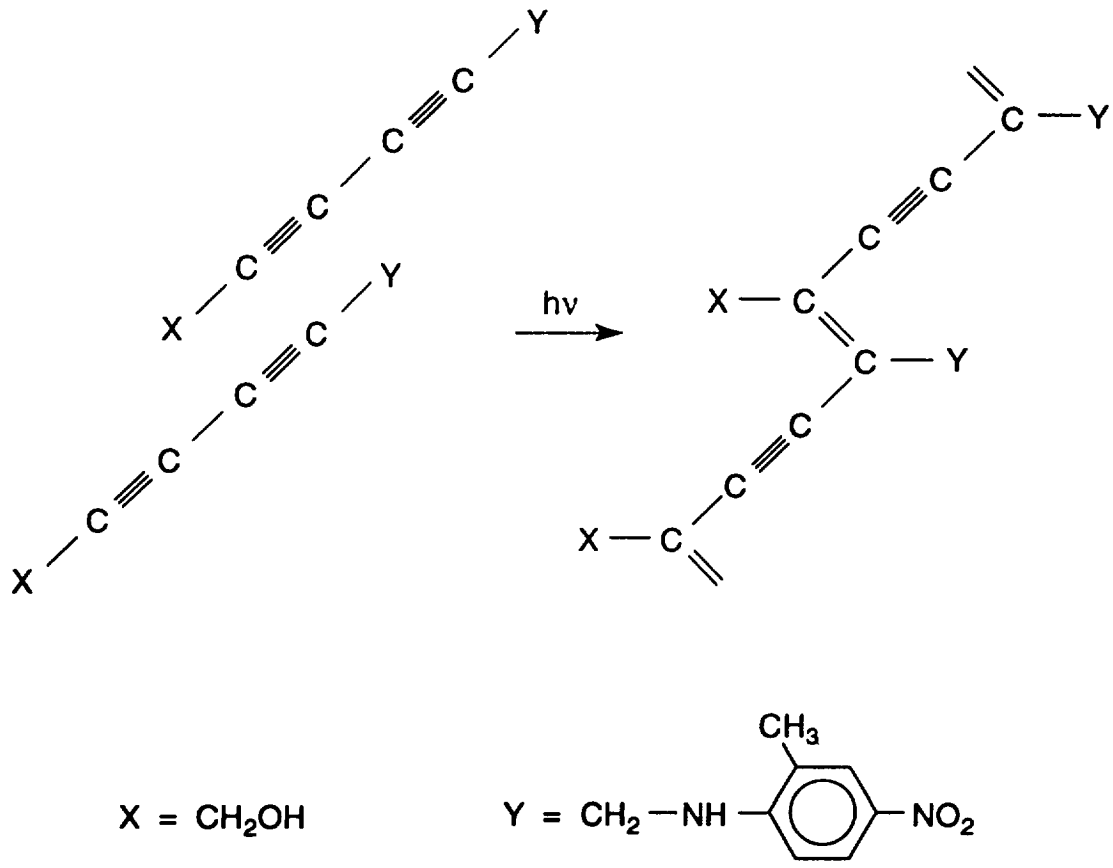
It is well-known that gravitational factors such as buoyancy-driven convection and sedimentation can affect chemical and mass transport processes in solution. One important aspect of polydiacetylene thin film photodeposition in solution, relevant to microgravity science, is that heat generated by absorption of UV radiation induces thermal density gradients that, under the influence of gravity, can cause fluid flows (buoyancy-driven convection). Additionally, changes in the chemical composition of the solution during polymerization may cause solutal convection. These fluid flows affect transport of material to and from the film surface and thereby affect the kinetics of the growth process. This manifests itself in the morphology of the resulting films; films grown under the influence of convection tend to have less uniform thicknesses, and can possess greater inhomogeneities and defects.

Specifically, polydiacetylene films photodeposited from solution, when viewed under a microscope, exhibit very small particles of solid polymer which get transported by convection from the bulk solution to the surface of the growing film and become embedded. Even when carried out under conditions designed to minimize unstable density gradients (i.e., irradiating the solution from the top), some fluid flow still takes place (particles remain present in the films). It is also possible that defect nulceation may be ocurring within the films or on the surface of the substrate; this, too, can be affected by convection (as is the case with crystal growth). Hence films grown in 1-g will, at best, still possess some defects. The objective of this proposal is to investigate, both in 1-g and in low-g, the effects of gravitational factors (primarily convection) on the dynamics of these processes, and on the quality, morphology, and properties of the films obtained.

Experimental Methods

The compound we have been investigating is a polydiacetylene derivative of 2-methyl-4-nitroaniline (MNA), a well-known organic nonlinear optical material. When a solution of the diacetylene monomer DAMNA in 1,2-dichloroethane is irradiated with longwave UV light through a transparent substrate, a thin polydiacetylene film (PDAMNA, see below) deposits on the surface of the substrate in contact with the solution.

DAMNA: **PDAMNA:**



X = CH_2OH

Y = CH_2—NH— —NO_2

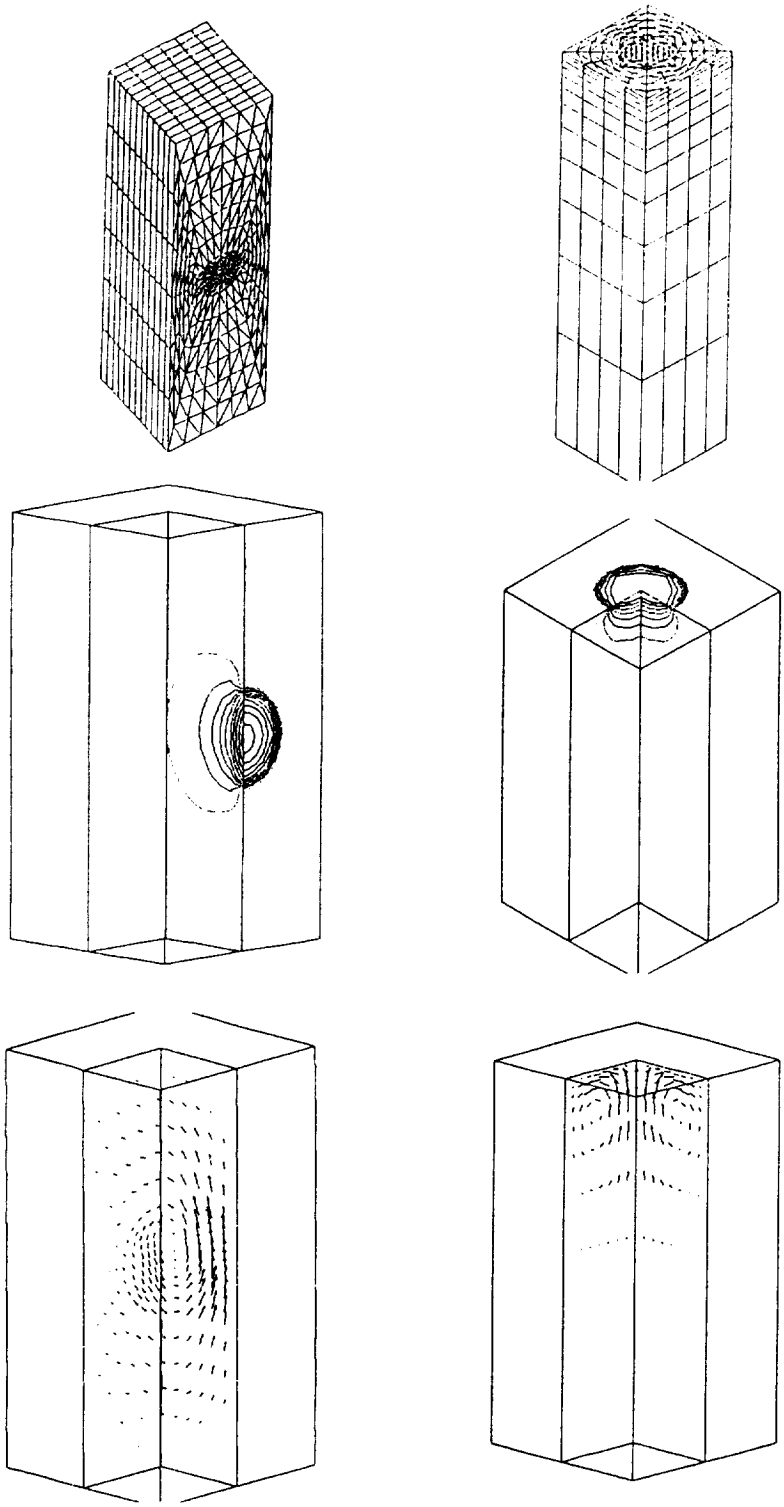
Studies on the effects of convection on photodeposition of PDAMNA films are proceeding on three fronts: numerical simulations of the fluid flow, experimental determination of the fluid flow, and in-situ spectroscopic ellipsometry studies of film deposition. Numerical simulations of the fluid flow are being conducted using FIDAP; the purpose of these studies is to ascertain the effects of variables such as cell geometry, orientation, light intensity, gravity, etc. on the pattern and intensity of the fluid flow. These studies are being complimented by experimental flow visualization studies using marker particles for simple cell geometries. Once the numerical simulations have been validated by the flow visualization studies; simulations can be performed with confidence for growth cell configurations where experimental determinations of the fluid flow are not possible.

Besides determining the fluid flow, we must also monitor film growth during PDAMNA film photodeposition in order to to discern how the fluid flow acually affects the deposition process. The technique we are employing is in-situ spectroscopic ellipsometry, which actually allows film growth to be monitored at the molecular level. Thus we should be able to observe how defects are formed in the films, whether they are transported from the bulk solution by convection, or nucleate within the film itself. We have designed and constructed a special cell for this purpose.

Preliminary Results

Kinetic studies on photodeposition of PDAMNA films from solution have shown that the rate of film growth is linear in light intensity and square root in monomer concentration. Furthermore under most growth conditions monomer is present in excess, and therefore the process is pseudo-zeroth order in concentration; i.e., the monomer concentration does not change appreciably. Thus we believe that the primary contributor to the fluid flow is thermal convection, and that solutal convection plays only a minor role. Hence at present we are only interested in studying thermal convection. Also, for the time being, we have chosen to ignore the effects of film growth on convection, the primary effect of which is to attenuate the UV light as the film thickness increases. The solution is heated via absorption of the UV radiation by the dissolved DAMNA molecules; both the solvent (1,2-dichloroethane) and the quartz cuvette are UV transparent. At the wavelength used (@366nm), it is the MNA portion of the DAMNA molecule that is responsible for the absorption, not the diacetylene. Thus we can use MNA as a model compound for DAMNA and thereby investigate thermal convection without the complication of film growth taking place. Typical monomer concentrations used for PDAMNA film photodeposition are on the order of 10^{-2} moles/liter, at these concentrations the absorption coefficient of the solution is on the order of $100cm^{-1}$ (for both DAMNA and MNA). Because the minimum fluid element used in the numerical simulations is a cube with 0.17mm sides, this means that 99% of the radiative heating takes place within those fluid elements adjacent to the cell wall upon which the UV light is incident. Therefore in our numerical model we treat the heating of the solution as if it were being heated by a source located at the inside wall of the growth cell.

Numerical simulations of the buoyancy-driven fluid flow have been conducted for a rectangular quartz cell with dimensions 1cm x 1cm x 4cm height containing a 10^{-2} mole/liter MNA solution in dichloroethane, with a circular UV beam 5mm in diameter incident upon either a vertical face or the top face of the cell. The calculations considered the beam to be centered on the appropriate face. Computations were performed for a range of beam intensities ranging from 0.25 Watt to 4.0 Watts total power, assumed to be uniformly distributed over the 5mm UV beam. The boundary and initial conditions used were appropriate for a system is at ambient temperature in which the walls of the cell are maintained at ambient temperature throughout the run. Because the solution is dilute, the thermodynamic parameters; i.e., heat capacity, thermal expansivity, kinematic viscosity, and thermal conductivity, for the MNA solution are taken to essentially be the same as those for the pure solvent, 1,2-dichloroethane. The values of these parameters were obtained from the literature. The resulting temperature and velocity fields are obtained through numerical solution to the conservation equations for fluid dynamics. The numerical code used employs the finite element approximation for solving the equations of motion. Figure 1 shows typical flow patterns and isotherms for the two heating modes; i.e., from the top and side of the cell. Also shown in Fig. 1 is the meshing employed in the numerical computations for each heating mode.



(a) (b)

Figure 1. The meshing used, the isotherms and the fluid velocity vectors for (a) side heating, and (b) top heating.

Experimental studies of the fluid flow are being conducted under the conditions described in the preceeding paragraph using poly(methacrylic acid) powder as marker particles. The flow pattern and velocities observed are in good qualitative agreement with the calculations; however, the magnitude of the experimental flow velocities (on the order of 10^{-1} cm/s) appears to be about a factor of 10 greater than the calculated velocities. We are currently in the process of finding the cause of this discrepancy, which we suspect is the manner in which the parameters were input into the code.

Preliminary measurements on PDAMNA film photodeposition using real-time in-situ spectroscopic ellipsometry have just begun using a spectroscopic ellipsometer coupled with an optical multichannel analyzer. A special cell was constructed for the purpose of studying PDAMNA film growth; the films are being grown onto glass substrates coated with a 5nm thick layer of gold. The gold is necessary in order to obtain reliable data because PDAMNA is a dielectric material; the coating is sufficiently thin that UV light can still penetrate into the solution and induce film growth. In the future the instrument configuration will be changed so that a compensator can be used, which should allow good data to be obtained without the gold coating. Also, in order to interpret the ellipsometry data, the optical constants of PDAMNA, specifically, the refractive index and the extinction coefficient, must be determined as a function of wavelength. Thus films of PDAMNA were grown on glass at several thicknesses and spectroellipsograms were obtained to determine these constants (assuming that the optical properties do not vary with thickness, which is expected to be the case).

Real-time in-situ spectroellipsograms were measured at various time intervals up to approximately 2 hours of film growth. Because of partial attenuation of the UV light by the gold, the rate of growth is quite slow. In order to determine the film thickness and/or void volume fraction, simulation of the experimental spectroellipsograms is attempted based on the optical constants of PDAMNA. These simulations are just now underway and results will be forthcoming.