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Journal of Crystal Growth 173 (1997) 172–181

## Effects of convection during the photodeposition of polydiacetylene thin films

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## Effects of convection during the photodeposition of polydiacetylene thin films

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### Abstract

In this work, we describe a preliminary investigation of buoyancy-driven heat transfer during the growth of thin films from solution following exposure to ultraviolet (UV) light. Irradiation of the growth cell occurs at various directions relative to gravitational acceleration. Through numerical computations, the steady-state flow and temperature profiles are simulated during the course of light exposure. Light-induced polymerization accompanies a heat transfer process through a fairly complicated recirculating flow pattern. A scaling analysis shows that buoyancy-driven velocities only reduce by a factor of 10 for gravity levels as low as  $10^{-2}g_0$ . Paley et al. observe what appears to be gravitationally sensitive particle development and inclusion in thin films using a photodeposition process. From this study, it is clear that production of homogeneous thin films would have to occur in the environment of a complicated flow pattern of recirculation with a nonuniform temperature distribution. Indeed, even when irradiation occurs from the top of the cell, the most stable stratified cell orientation, defects remain in our films due to the persistence of buoyancy-driven convection. To achieve homogeneity, minimal scattering centers, and possible molecular order, photodeposition of polymer films by UV light exposure must proceed in a reduced-convection environment. Fluid mechanics simulations are useful for establishing gravitational sensitivity to this recently discovered process (patent # 5,451,433) for preparing thin films having quite promising nonlinear optical characteristics.

### 1. Introduction

In recent years, there has been a great deal of interest in the use of organic materials in the development of high-efficiency optoelectronic and photonic devices. There are many possibilities among organics which allow considerable flexibil-

ity in the design of unique structures having a variety of functional objectives. The use of nonlinear optical (NLO) organic materials as thin film waveguides allows full exploitation of their desirable qualities by permitting long interaction lengths and large power densities with modest power input [1]. Organics have many features that make them desirable for use in optoelectronic devices such as high second- and third-order nonlinearities, flexibility of molecular design, and damage

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resistance to optical radiation. However, their use in devices has been hindered by processing difficulties for crystals and thin films.

One very promising class of organic compounds for NLO applications are polydiacetylenes, which are novel in that they are highly conjugated polymers which can also be crystalline [2]. Polydiacetylenes offer several advantages over other organic materials because (a) their highly conjugated electronic structures make them capable of possessing large optical nonlinearities with fast response times; (b) they can be highly ordered, and indeed crystalline, which is essential for optimizing their NLO properties; and (c) their polymeric properties allow their formation into thin films which are useful for device fabrication. There are several methods in use to prepare thin films, such as Langmuir–Blodgett [3–5], growth from sheared solution or melt [6–8], Vapor deposition [9–11], and melt growth between glass plates [12]. Epitaxial growth onto ordered organic and inorganic substrates, and variations in processing conditions are useful for preparing highly oriented polydiacetylene films. The relationship between processing conditions and uniformity in thickness, degree of orientation, and NLO properties is important. In this paper, we discuss gravitational influences during a novel technique for growing thin films which involves exposing a transparent substrate, in contact with diacetylene monomer solution, to ultraviolet (UV) light from the backside. A polymer film deposits on the side of the substrate in contact with monomer in solution.

Polydiacetylenes are generally prepared by synthesizing diacetylene monomers, growing crystals or thin films of the monomers, and then polymerizing these monomers, usually in the solid state, by exposure to UV light or gamma rays [13]. Of interest is the diacetylene monomer 6-(2-methyl-4-nitroanilino)-2,4-hexadiyn-1-ol (DAMNA). In our process, thin amorphous films of the corresponding polydiacetylene (PDAMNA) deposit through polymerization of the diacetylene monomer in solution by exposure to UV light (Fig. 1) [14]. The absorption of UV radiation by the solution can result in fairly intense fluid flows which affect film quality. The flow fields and temperature distributions during the polymerization process by expo-

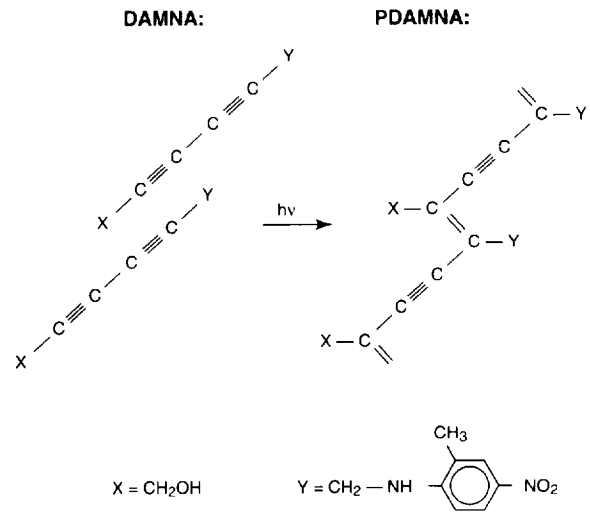


Fig. 1. The diacetylene monomer, 6-(2-methyl-4-nitroanilino)-2,4-hexadiyn-1-ol (DAMNA) photo-polymerizing to form PDAMNA.

sure to UV light details the nature of gravitational influences on this process.

Our approach is to investigate the transient, three-dimensional behavior of flow fields and temperature distributions through buoyancy-driven convection under normal gravity with various orientations of the growth chamber. Since the onset of steady-state conditions occurs after 10 s, and the duration of photodeposition is about 2 days, our interest in this paper is to report the steady-state flow fields and temperature distributions. Steady-state conditions correlate most meaningfully to the experimental data. Observations on the initial transient will appear in a future communication. The chamber contains a solution of DAMNA in 1,2-dichloroethane and convection proceeds from exposure to UV light. Good quality thin films elude growth from solutions absent of uniform flow fields and homogeneous temperature distributions near the substrate surfaces.

## 2. Numerical simulation of fluid flows

We consider a cylindrical chamber with a radius of  $r_0$  and height  $L$ . Fig. 2 shows the geometrical

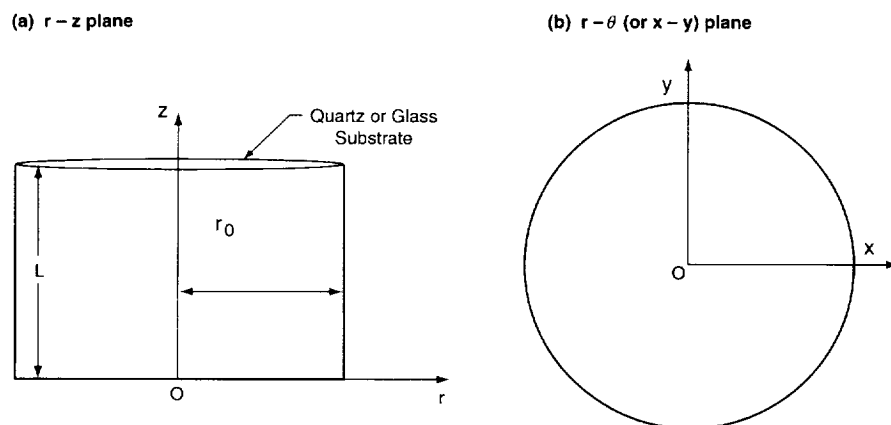


Fig. 2. Geometrical illustration of cylindrical chamber for mathematical modeling (a) in an  $r-z$  plane, and (b) in an  $r-\theta$  plane.

configuration of the test chamber. For the purpose of considering the mathematical formulation, we adopt cylindrical coordinates  $(r, \theta, z)$  with corresponding velocity components  $(u, v, w)$ , and components of gravity acceleration  $(g_r, g_\theta, g_z)$ . Fig. 2a and Fig. 2b show the geometrical configuration of the cylindrical chamber in an  $r-z$  plane and an  $r-\theta$ , plane, respectively. The chamber is made of aluminum and operates at room temperature taken as 25°C. The chamber is filled with a solution of DAMNA in 1,2-dichloroethane, and at least one wall, through which UV radiation enters the cell, is UV transparent (quartz) and serves as the film substrate. Absorption of UV by the film itself is neglected in this preliminary study. The flow profiles and temperature distributions in the monomer solution are mainly governed by natural convection and driven by the absorption of UV radiation. The governing equations are time-dependent, three-dimensional incompressible continuity, momentum (full Navier–Stokes equations), and energy equations incorporating Boussinesque assumptions [15].

The heat source is absorption of UV radiation, given by the Beer–Lambert law [16]. In this preliminary analysis we are primarily interested in steady-state conditions, which develop in 10 s. Because of this, and the presence of excess monomer, the monomer concentration does not decrease appreciably until after several hours of irradiation

[17]. We can therefore treat monomer concentration as constant for these calculations and ignore the concentration dependence of the absorption coefficient. The expression for the rate of heat generation per unit area at depth  $z$  is

$$q_0 \{1 - \exp[-\alpha(L - Z)]\},$$

where  $\alpha$  is the UV absorption coefficient (or decay coefficient) of DAMNA in 1,2-dichloroethane (2.5 mg/ml)  $\approx 150 \text{ cm}^{-1}$ ,  $L$  the height of container and  $q_0$  is the intensity of UV radiation ( $\text{W/cm}^2$ ).

The initial condition is that the system is at room temperature (25°C), and the boundaries are the inner walls which remain at 25°C throughout the process (no penetration and no slip for flow fields).

In this study, a cylindrical container, as illustrated in Fig. 2, has the following specifications:  $2r_0 = 1.5 \text{ cm}$  and  $L = 1.0 \text{ cm}$ . Because the solution is very dilute, solution physical parameters are primarily estimates of the solvent, 1,2-dichloroethane at 25°C: solution density  $\rho = 1.2 \text{ g/cm}^3$ , kinematic viscosity  $\nu = \mu/\rho = 0.33 \times 10^{-2} \text{ cm}^2/\text{s}$ , coefficient of thermal expansion for solution  $\beta = 1.2 \times 10^{-3} \text{ K}^{-1}$ , heat conduction coefficient  $\kappa = 1.03 \times 10^{-3} \text{ W/cm} \cdot \text{K}$ , and constant pressure specific heat  $c_p = 1.0 \text{ J/g K}$ ; gravity acceleration  $g_0 = 9.81 \text{ m/s}^2$ .

A numerical algorithm [18–20] using a finite difference approach was used to determine the time-dependent, three-dimensional flow profiles

and temperature distributions leading to our reported steady-state conditions. Grid points of  $21 \times 34 \times 10$ , respectively, along  $(r, \theta, z)$  coordinates were used in this numerical computation. The level of UV irradiation intensity for all computations was  $q_0 = 1.00 \text{ W/cm}^2$ . The chamber orientation varies according to  $\psi = 0^\circ$  (irradiation from the top),  $90^\circ$  (irradiation from the side), and  $180^\circ$  (irradiation from the bottom) by rotating the  $z$ -axis relative to gravitational acceleration. We observe flow profiles in the cylinder in the orthogonal planes,  $\theta = 0$ – $180^\circ$  and  $\theta = 90$ – $270^\circ$  to investigate the characteristics of convection-driven flows and temperature profiles.

### 2.1. $\psi = 180^\circ$

The steady-state convection-induced flow field upon bottom irradiation of the reaction chamber ( $\psi = 180^\circ$ ) is illustrated in Fig. 3. We would intuitively expect quite intense flow in this orientation. The convection-induced flow vector depiction in Fig. 3a is in an  $r$ - $z$  plane. Note the two recirculation zones that form about the  $z$ -axis. Fig. 3b shows steady-state convection-induced outflow in the vicinity of the quartz substrate (at  $z = 0.97 \text{ cm}$ ) in the  $r$ - $\theta$  ( $x$ - $y$ ) plane.

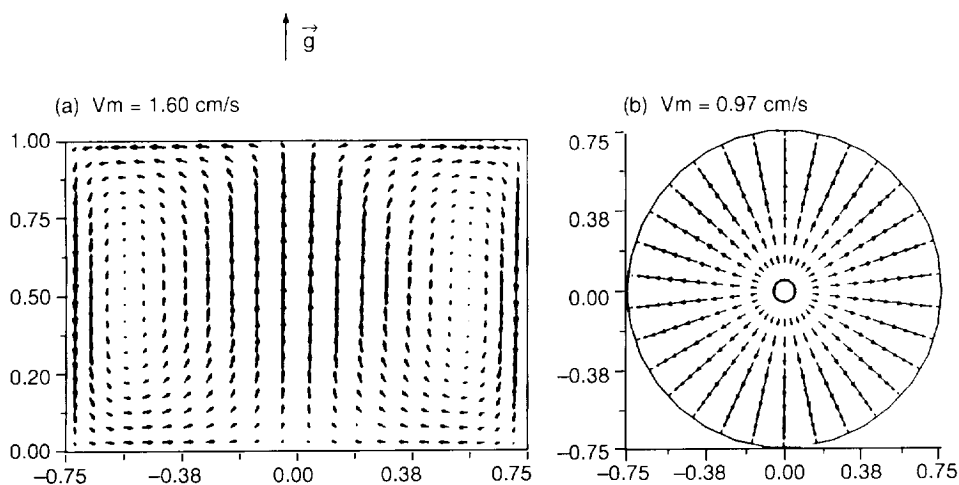


Fig. 3. Steady-state flow profile due to UV irradiation from the bottom of the chamber ( $\psi = 180^\circ$ ) (a) in the  $r$ - $z$  plane coincident with  $\theta = 0$ – $180^\circ$  and (b) in the  $r$ - $\theta$  plane at  $z = 0.97 \text{ cm}$ .

Fig. 4a and Fig. 4b show steady-state temperature profiles due to induced convection in the  $r$ - $z$  plane coincident with  $\theta = 0$ – $180^\circ$ , and in the  $r$ - $\theta$  plane at  $z = 0.97 \text{ cm}$ , respectively. The curves in Fig. 4a and Fig. 4b are the isothermal lines with the indicated temperatures in  $^\circ\text{C}$  at the corresponding locations. Figs. 3 and 4 suggest that bottom irradiation of the chamber induces pronounced temperature and flow profiles possibly harmful to developing order in photodeposited films during ground processing. In this orientation, it may be possible to enhance the pattern of film heterogeneity during unit gravity processing by maximizing irradiation intensity.

### 2.2. $\psi = 0^\circ$

The steady-state convection-induced flow fields upon top irradiation of the reaction chamber ( $\psi = 0^\circ$ ) is illustrated in Fig. 5a and Fig. 5b. The figures show convection-induced flow vectors in an  $r$ - $z$  plane, and in the  $r$ - $\theta$  plane at  $z = 0.97 \text{ cm}$ , respectively. Although the maximum flow velocity is quite small, Fig. 5a and Fig. 5b illustrate the possibility of an interesting process. During irradiation of monomer solution through the quartz substrate, there is no absorption of energy by the

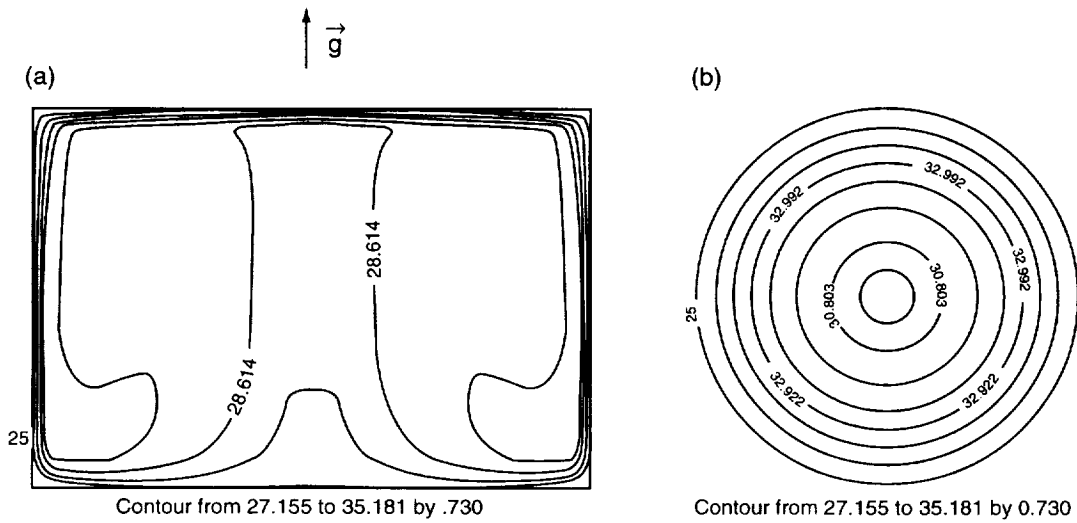


Fig. 4. Steady-state temperature profile due to UV irradiation from the bottom of the chamber ( $\psi = 180^\circ$ ) (a) in the  $r$ - $z$  plane coincident with  $\theta = 0$ - $180^\circ$  and (b) in the  $r$ - $\theta$  plane at  $z = 0.97$  cm.

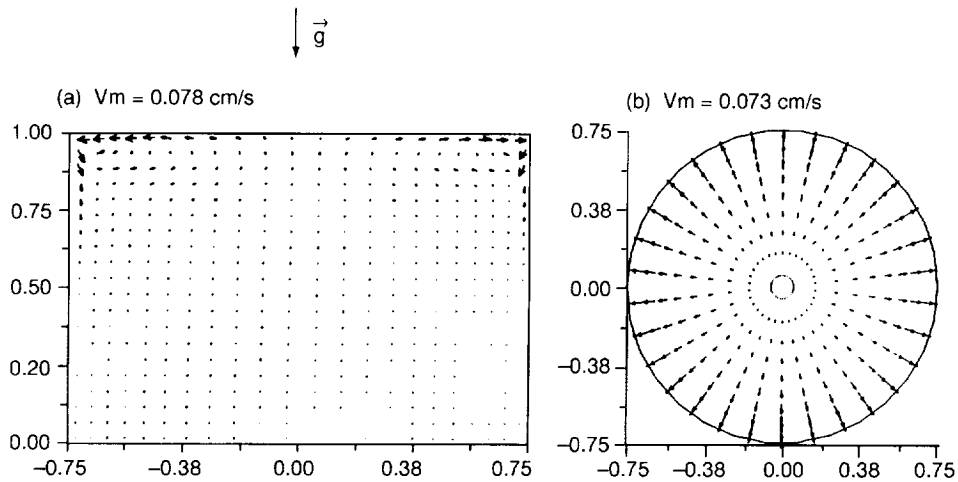


Fig. 5. Steady-state flow profile due to UV irradiation from the top of the chamber ( $\psi = 0^\circ$ ) (a) in the  $r$ - $z$  plane coincident with  $\theta = 0$ - $180^\circ$  and (b) in the  $r$ - $\theta$  plane at  $z = 0.97$  cm.

quartz since it is transparent to UV light. However, there is absorption by the solution in contact with the window. Therefore, for  $\psi = 0^\circ$ , because of the cool quartz and, to some penetration depth, hotter solution, we expect an unstable thermal gradient in a thin fluid layer adjacent to the quartz window

[21]. There is a small radial outflow along the horizontal direction at the top within a thin layer near the quartz substrate in an  $r$ - $\theta$  plane.

Fig. 6a and Fig. 6b show steady-state temperature profiles resulting from top irradiation in the  $r$ - $z$  plane coincident with the plane  $\theta = 0$ - $180^\circ$



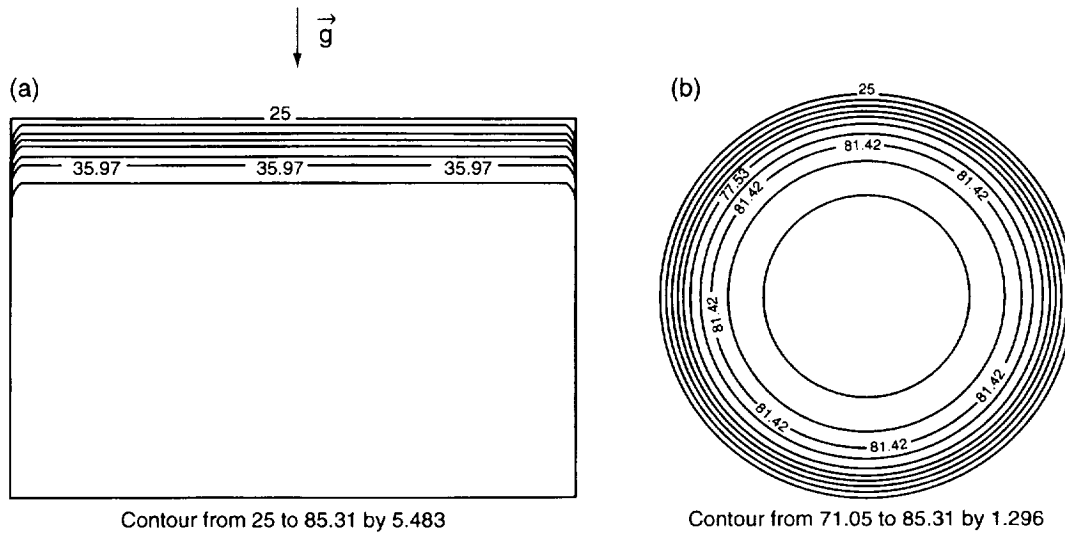


Fig. 6. Steady-state temperature profile due to UV irradiation from the top of the chamber ( $\psi = 0^\circ$ ) (a) in the  $r-z$  plane coincident with  $\theta = 0-180^\circ$  and (b) in the  $r-\theta$  plane at  $z = 0.97$  cm.

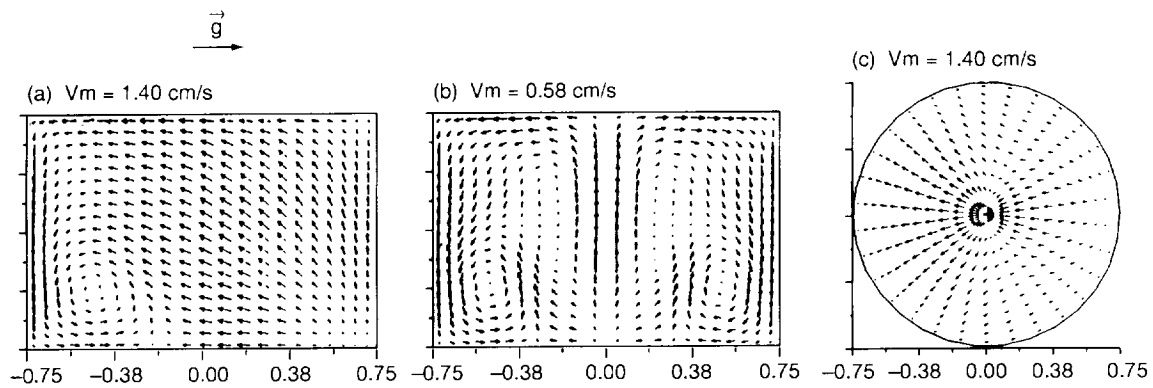


Fig. 7. Steady-state flow profile in an  $r-\theta$  plane due to UV irradiation from the side of the chamber ( $\psi = 90^\circ$ ) at intensity  $1.0 \text{ W/cm}^2$ . (a) At  $\theta = 0-180^\circ$ , (b) at  $\theta = 90-270^\circ$ , and (c) in the  $r-\theta$  plane at  $z = 0.97$  cm.

and in the  $r-\theta$  plane at  $z = 0.97$  cm, respectively. There is a very small variation in the temperature distribution. The medium is otherwise stably stratified.

### 2.3. $\psi = 90^\circ$

In the case of convection driven by side irradiation ( $\psi = 90^\circ$ ), the quartz window orientation

through which the radiation passes is  $90^\circ$  relative to the  $z$ -axis. An  $r-z$  cross section coincident with the plane  $\theta = 0-180^\circ$  illustrates typical convection induced by side heating (Fig. 7a). On the other hand, Fig. 7b illustrates the  $r-z$  plane coincident with the plane  $\theta = 90-270^\circ$ , and shows convection induced by heat flows from the top. Gravitational acceleration is perpendicular to the flow direction (perpendicular to the figure shown). Fig. 7c shows

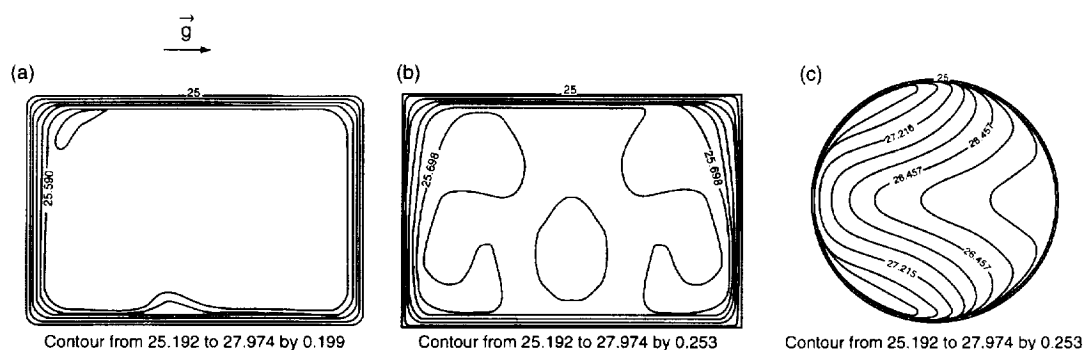


Fig. 8. Steady-state temperature profiles due to UV irradiation from the side of the chamber ( $\psi = 90^\circ$ ) (a) in the  $r$ - $z$  plane coincident with  $\theta = 0$ - $180^\circ$ , (b) in the  $r$ - $z$  plane coincident with  $\theta = 90$ - $270^\circ$ , and (c) in the  $r$ - $\theta$  plane at  $z = 0.97$  cm.

steady-state flows in an  $r$ - $\theta$  plane in the vicinity of the quartz substrate (at  $z = 0.97$  cm).

Fig. 8a and Fig. 8b show the steady-state temperature profiles in the  $r$ - $z$  plane coincident with  $\theta = 0$ - $180^\circ$ , and  $\theta = 90$ - $270^\circ$ , respectively, while the reaction chamber is tilted  $90^\circ$  with respect to gravitational acceleration. Fig. 8c shows the steady-state temperature profile in the vicinity of the quartz substrate.

### 3. Experiments: $\psi = 0^\circ$ , $90^\circ$ , and low-gravity

The chambers constructed for carrying out photodeposition of PDAMNA thin films from solution onto small round substrate disks are of approximately the same geometry as described in the numerical model. To grow thin films onto quartz disks (or any UV transparent substrate), the chambers are filled with a solution of DAMNA in 1,2-dichloroethane (approximately 2.5 mg/ml = 0.01 mols/l), and irradiated through the substrate with long wavelength (365 nm) UV light. As the solution is irradiated, a photopolymerization reaction occurs and a thin PDAMNA film deposits on the inside surface of the substrate as described in the earlier sections. Besides the heat transfer process as modeled, we also suspected that there could be a solutal contribution to the fluid flow. That is, some solutal convection could occur due to depletion of monomer in the vicinity of the growing film which can give rise to variations in

monomer concentration and subsequently induced density gradients. However, at the low monomer concentrations we are considering, there is very little change in solution density with monomer concentration, and therefore, we expect solutal convection to be minimal. Also, as stated previously, monomer concentration varies little during early stages of photodeposition. In order to begin to sort out dominating factors driving convection and flow patterns, we deposited PDAMNA films while tilting the chamber  $z$ -axis (Fig. 2) and irradiating the solution at  $0$  and  $90^\circ$  relative to gravitational acceleration.

The most obvious indication of convection, experimentally, has been the observation of particles of solid polymer embedded in the films when viewed under an optical microscope. These particles form when polymer chains in the bulk solution collide due to convection and coalesce into small solid particles on the order of a few hundredths to tenths of a micron in size. Because these particles are so 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 incorporated. In the case where the chamber is vertical and the solution is irradiated from the top ( $\psi = 0^\circ$ ), the mathematical model reflects that convection is at a minimum. This is also the case experimentally (Fig. 9b). Even though convection is minimal, there are still some solid particles embedded in the film following

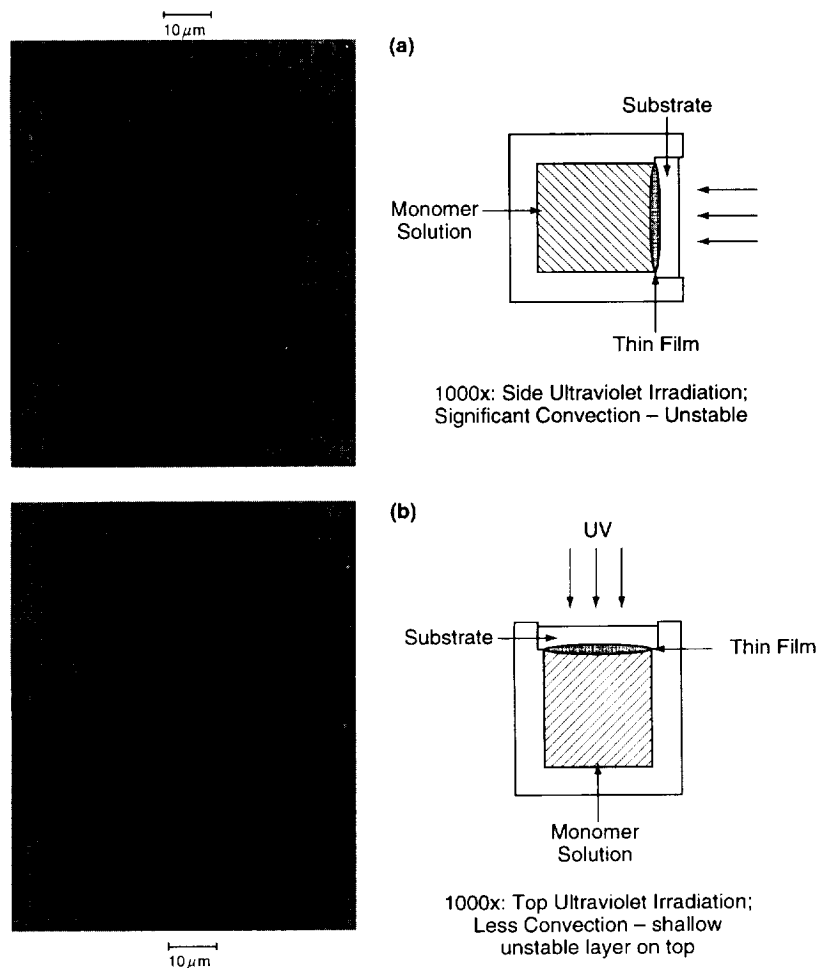


Fig. 9. PDAMNA particles embedded due to convectively induced polymer chain collisions and transport to film surface. The corresponding illustrations are: (a) side irradiation ( $\psi = 90^\circ$ ) where there is significant convection (1000 $\times$ ) and (b) top irradiation ( $\psi = 0^\circ$ ) where convection is considerably less (1000 $\times$ ).

irradiation from the top of the chamber. This may occur because the model predicts a thin unstable layer having an outward flow profile with flow vector magnitudes increasing with beam intensity. Additionally, the radial temperature gradient can give rise to convection. In the case where the chamber is perpendicular to gravitational acceleration, and the solution is irradiated from the side ( $\psi = 90^\circ$ ), the mathematical model predicts significant flows consistent with side heating of the sample. This result is also consistent with the experiment (Fig. 9a). There is a far greater concentra-

tion of particles in films grown in this horizontal orientation than in the case of top irradiation.

Last, we recently 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 and limitations of the flight hardware, results varied somewhat from one sample to another. However, as seen from Fig. 10, the best space-grown film clearly exhibits

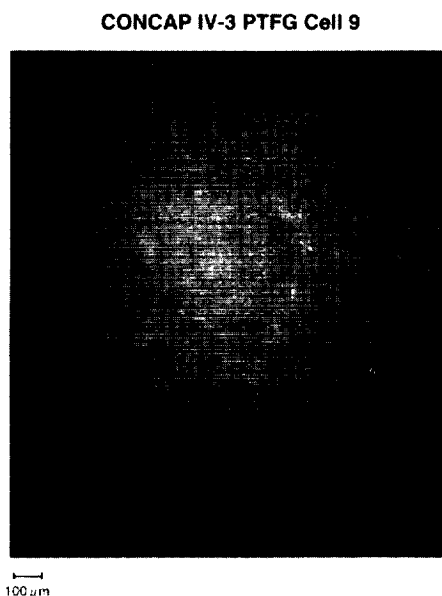


Fig. 10. PDAMNA films grown by photopolymerization on the shuttle Endeavor (STS-69; CONCAP-IV).

fewer particles (virtually none) than the best ground-based films. These few particles may have resulted from slight mixing in the solution caused by the orbiter motion or, possibly, they may have nucleated on the surface of the film itself. Nonetheless, the preliminary 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. We are currently planning more sophisticated space experiments that should ensure greater reproducibility from one sample to another, as well as allow direct observation of fluid flows and film growth during photodeposition. Measurements of film homogeneity, surface roughness, NLO properties, etc., will be the subject of future experiments.

#### 4. Discussion and conclusion

The calculations accurately predict the gross quality of polymer films produced by the novel process of photodeposition. The evidence is strong that heat absorbed by the solution induces buoy-

ancy-driven convection which clearly affects film quality. Even during photopolymerization in the most stable reaction chamber configuration, i.e. top irradiation, it is impossible to avoid particle incorporation in the film as demonstrated by the model and the experiment. However, photo-deposition conducted in the reduced-buoyancy environment of space shows promise for eliminating these defects. The particles act as scattering centers which are a direct impediment to high quality waveguiding and photonic applications. However, it is clear that control of driving forces for convection in addition to rational approaches to molecular engineering could improve order and quality in photodeposited films.

More precise estimates of the pattern of film homogeneity as a function of reaction chamber orientation will proceed by mapping the surfaces of photodeposited films using ellipsometry, optical microscopy, and techniques for determining molecular orientation in the film. As resolution in topography progresses, more specific correlation with predicted patterns on the basis of flow profiles and temperature distributions will be likely.

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