Gravitational Effects On the Morphology and Kinetics of Photo-Deposition 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 photo-deposition 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 transparent 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. 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.

Microgravity Relevance

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 photo-deposition 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 photo-deposited 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). This may result from penetrative convection, which occurs because a very shallow thermally unstable layer near the film sits above a more stable layer; convection induced in this unstable layer can penetrate into the

stable layer. Additionally, defect nucleation may be occurring within the films or on the surface of the substrate; this can also 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 diffusion-controlled environment of microgravity would greatly reduce convection and allow comparative studies of polydiacetylene thin film growth under high and low-g conditions.

Methods and Results

Understanding the effects of convection on the dynamics of the photo-deposition process, and on the nature and properties of the polydiacetylene films obtained is the central tenet of this proposal. We have synthesized and characterized a diacetylene derivative of MNA, a well-known organic NLO material, and prepared thin films of the corresponding polydiacetylene by irradiation of monomer solutions through glass or quartz substrates. Fundamental studies (ground-based) on the kinetics, photo-chemistry and mechanism of this process are ongoing. We have determined that the rate of film growth is linear in light intensity and square root in monomer concentration. A determination of the kinetics of particle formation in solution is currently underway. A simple, preliminary low-g experiment was conducted on a GAS can aboard *Endeavor* in late 1995. Films were grown in low-g and compared to ground-control samples. While the results varied somewhat among flight samples (probably due to extraneous Shuttle accelerations), the best polydiacetylene films grown in space exhibit virtually no defects, and are superior to the best ground-based films. This strongly suggests that convection is a significant factor in affecting film quality.

Numerical modeling studies of the fluid flow as a function of gravity, light intensity, cell geometry, etc. are being conducted. These studies are complemented by ground-based experimental studies using flow visualization methods, and analyses of the morphology, microstructure, and properties of the films. Techniques such as interferometry, flow visualization, in-situ ellipsometry, optical and atomic force microscopy, UV-Vis and FTIR spectroscopy, and nonlinear optical characterizations are being employed.

Numerical simulations performed thus far indicate that under radiation intensities of 1 watt/cm^2 the maximum flow velocity is on the order of 10^{-2} cm/s for side irradiation and on the order of 10^{-3} cm/s for top irradiation, which given that film growth occurs over hours, is significant. The computations also predict that the maximum velocity varies almost linearly with light intensity. Preliminary flow visualization experiments using marker particles at least qualitatively corroborate the simulations in that the flow pattern predicted is observed. We are currently in the process of measuring the flow velocities experimentally in order to quantitatively verify the computations. We have also constructed a special cell which allows film growth to be monitored in-situ using spectroscopic ellipsometry. This technique allows the films to be monitored at the molecular level during photodeposition; thus we should be able to observe defect formation as it occurs.

Once convective effects are discerned in 1-g, the next step will be to propose mid-deck flight experiments (more sophisticated than ones possible on the GAS can) to determine the effects of the reduced-convection, diffusion-controlled environment of microgravity on film growth.