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INVESTIGATION OF SOLUTION POLYMERIZATIONS IN MICROGRAVITY AND 1G.

Prepared By: Alvin P. Kennedy, Ph.D.

Academic Rank: Associate Professor

Institution and Department   North Carolina A&T State University
                                      Department of Chemistry

NASA/MSFC

      Office: Space Sciences Laboratory
      Division: Microgravity Science & Applications

MSFC Colleagues: Donald Frazier, Ph.D.
                                      Steve Paley, Ph.D.
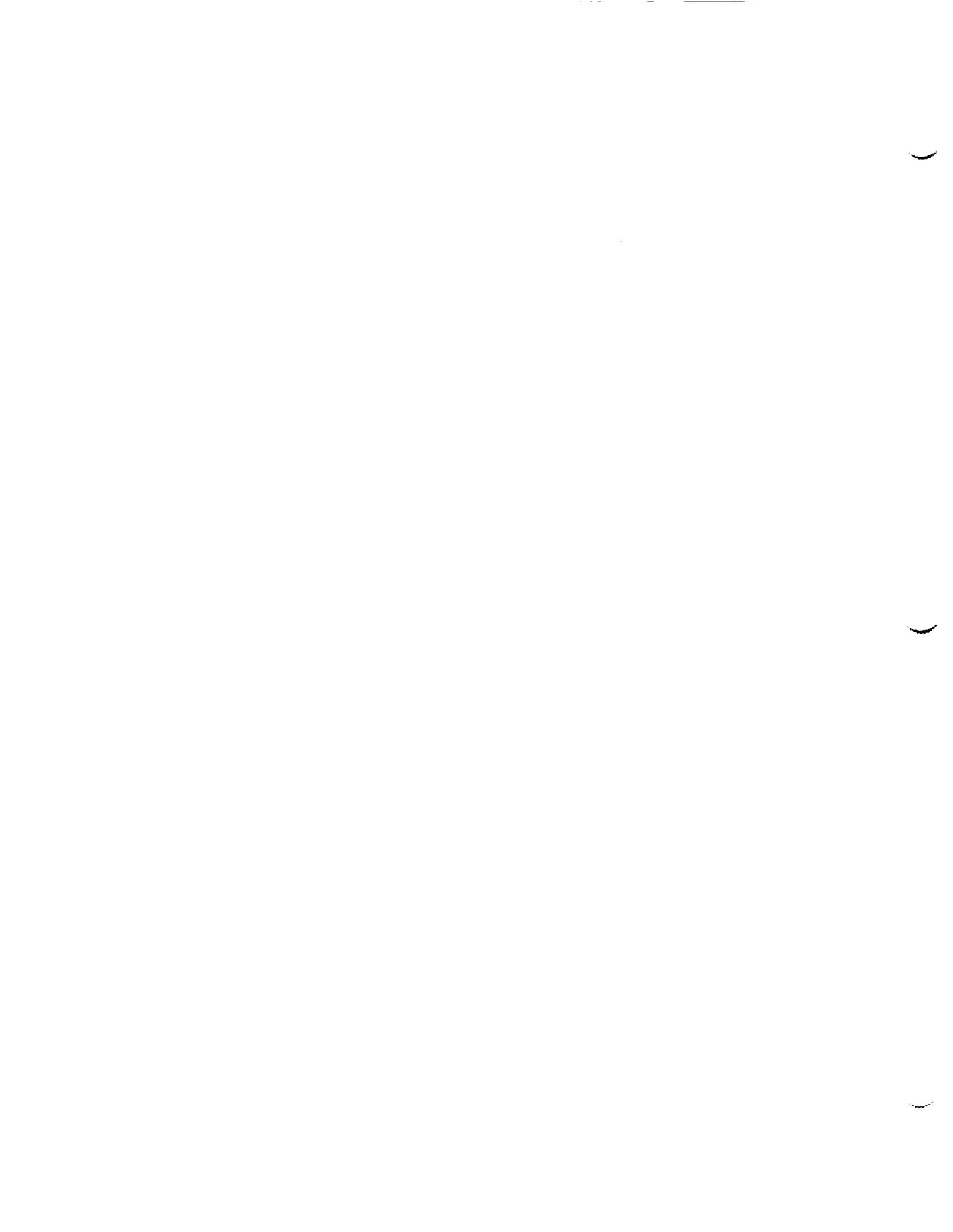
Introduction

Only a few investigations have been performed on polymer reactions in a microgravity environment. The majority of microgravity investigations have involved biological and inorganic materials and processes. Polymeric systems have not been extensively investigated because most polymers are too viscous for any microgravity effects such as convection or sedimentation to be important.(3) However in the case of solution phase polymerization these effects are more important. Resent results from two separate solution polymerization experiments have indicated the importance of gravitational effects on polymerization.

Recently a UV polymerizable prepolymer solution of Cyclotene was flown on a KC-135 flight. The sample was irradiated for 15 sec intervals at 0.2 G for 40 times. A control sample was irradiated under similar conditions using the same UV cell on the ground. The low gravity UV polymerized sample was a yellowish fluid and similar in viscosity to the starting prepolymer solution. The 1-G sample was dark orange with brown inclusions, and had begun to develop a crosslinked network structure. It had a much higher viscosity than the low gravity sample. Typically in thermosets sedimentation and phase separation occur near the gel point and the high molecular weight polymer separates from the liquid monomer or solvent. These processes determine the variation in molecular weight which is obtained in an earth based environment. Since this process is a result of the gravitational effect on the higher molecular weight material, higher molecular weight polymers and possibly different polymer morphologies might be obtained under microgravity conditions. Similar effects can occur during the polymerization of crystalline polydiacetylene (4). Dielectric spectroscopy has been used to monitor the solution polymerization of polydiacetylene.

Many different techniques have been used to investigate the polymerization process, however dielectric spectroscopy provides a simple yet powerful technique for following the polymerization process from monomer to polymer. Dielectric spectroscopy has been used to study a variety of thermoset resins, however most research has been conducted on epoxy thermosets. The dielectric behavior of epoxy resins can be adequately described by the Debye model (2), in which the dielectric constant ε' is given by:

Eq. 1
$$\varepsilon' = \varepsilon_u + \frac{\left(\varepsilon_r - \varepsilon_u\right)}{1 + \left(\omega\tau\right)^2}$$

where ε_u and ε_r are the unrelaxed and the relaxed dielectric constants, respectively, ω is the angular frequency given by $\omega = 2\pi f$, and τ is the characteristic relaxation time. The dielectric loss ε'' is given by:

Eq.2
$$\varepsilon'' = \frac{\sigma}{\omega \varepsilon_o} + \frac{(\varepsilon_r - \varepsilon_u)\omega\tau}{1 + (\omega\tau)^2}$$

where σ is the ionic conductivity, and ε_0 is the permittivity of free space. The first term represents the ionic conductivity of the material and becomes dominate at low frequencies. This term will vary with the viscosity of the material and the ionic concentration, which can also change during cure. The second term is the dipolar component of the dielectric loss. This term should change as the network forms and as the viscosity changes. A maximum is observed in the dielectric loss spectra when $\omega\tau = 1$, and experimentally the relaxation time can be determined from the loss peak. In the case of a curing resin, ε_r and ε_u would correspond to the neat resin and cured polymer, respectively. This model is based on a static number of dipoles which respond to variations in the applied frequency. Although of the dipoles in the monomer and curing agent are consumed during the polymerization process, this model has worked well for epoxy resins (1,5). How applicable this model is in describing the solution polymerization of polydiacetylene will have to be determined.

Experimental

The dielectric measurements were made using a HP4274A LCR meter. The unit measures capacitance and dissipation factor (tan D) from 100 Hz to 100 kHz in steps. The LCR meter was interfaced to the PC using Labview software. The program allows measurements to be taken at 30 sec or larger intervals for the duration of the run. Typical runs used 5 minute intervals for at least 24 hours. Measurements were taken at 1, 2, 4, 10, 20, 40, and 100 kHz. Gold plated glass interdigitated electrodes were purchased from DekDyne and used to measure the impedance of the solutions. A 1000W UV lamp was used at a distance of 4-5" from the cell.

Two different sample cells were used. For the bulk measurements a rectangular aluminum cell was used. It consisted of a solid rear block with small holes drilled for the leads to feed through and a front cover with a rectangular area drilled out to permit irradiation through a glass slide. The electrode was positioned facing the UV source and glued to the back of the cell with RTV rubber. Leads were soldered onto the electrode with either silver paste or indium solder. The indium solder was more resistant to solvent

attack. In this position the electrode was measuring the bulk solution. Enough sample was added to cover the electrode but not fill the cell. The feed through holes were sealed with RTV rubber. A brown solid was always observed near the solder joints of the electrode. It appeared to be vapor deposited crystalline polydiacetylene. Attempts to attached the electrode face up on the glass slide and irradiate through the back were unsuccessful because the total absorbance of the slide and electrode was too high for reaction to occur. For surface polymerization the electrode was attached face down on to a cylindrical aluminum test cell using a tie down. The sample was injected through a hole in the back and sealed with RTV rubber after the cell was filled. Electrical contact was made using alligator clips.

Results and Discussion

Results for the bulk experiments are shown in figure 1. Data was collected for the first 40 minutes without irradiation. During this time the capacitance and dissipation factor remained nearly constant. As soon as the lamp was turned on there was a large increase in the capacitance and dissipation factor for the lower frequencies. This indicates that the changes are due to the photopolymerization reaction. The bulk sample has a peak in the capacitance at 590 minutes for the 1 kHz data (Fig. 1A). The dissipation factor increases rapidly and goes off scale for the 1kHz data in the first 250 minutes and then decreases again. There is no peak observed in the capacitance data at 100 kHz (figure 1B). The initial decrease in the 100 kHz data is due to the partial heating of the cell by the UV lamp. This change was also observed when only the solvent was heated. The dissipation factor raises rapidly then levels off for 300 minutes and peaks near 590 minutes at the same time observed in the 1 kHz capacitance data.

Figure 1A and 1B
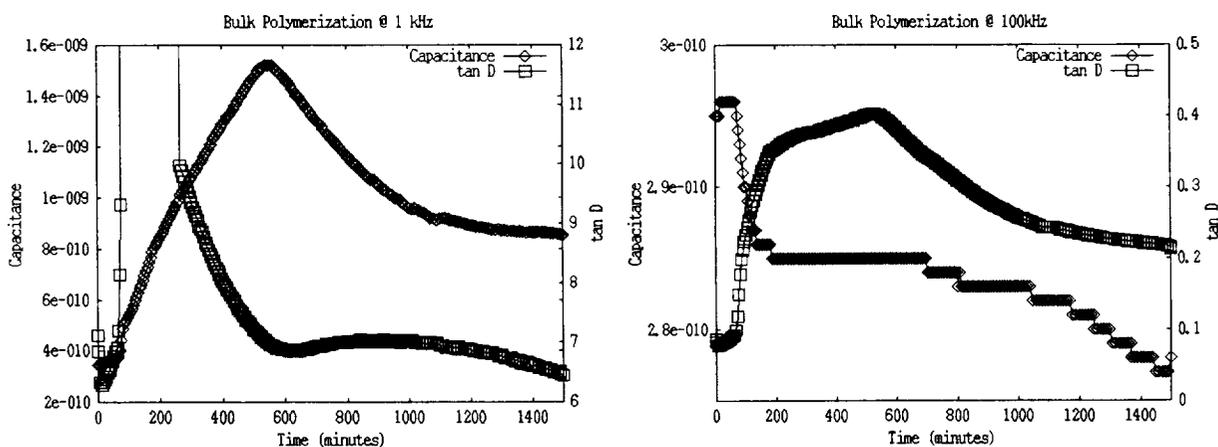
The peak in the capacitance at 590 minutes is present at 10 kHz but completely diminished at 20 kHz and above. The peak in the dissipation factor at 200 minutes is present in the 2 kHz but has diminished in size at 4 kHz. And the peak in the dissipation factor at 590 minutes is present at 4 kHz and higher frequencies. Since the observed peaks occur at the same time it suggests a single process is affecting the different frequencies.

The results for the surface experiments are shown in figure 2. There is an increase in the capacitance during the first 400 minutes at 1 kHz, after which the capacitance levels off instead of decreasing as was observed in the bulk data (figure 2A). The dissipation factor has a peak at 200 minutes similar to the one observed in the bulk data. The decrease in intensity is probably due to the smaller available surface area of the cylindrical cell. The capacitance at 100 kHz is exactly like the bulk data (figure 2B). And suggests that the reaction is not producing any products which are active at the higher frequency. The dissipation factor has the same form as the capacitance at 1 kHz. However the dissipation factor clearly decreases at longer times at 100 kHz.

Figure 2A and 2B
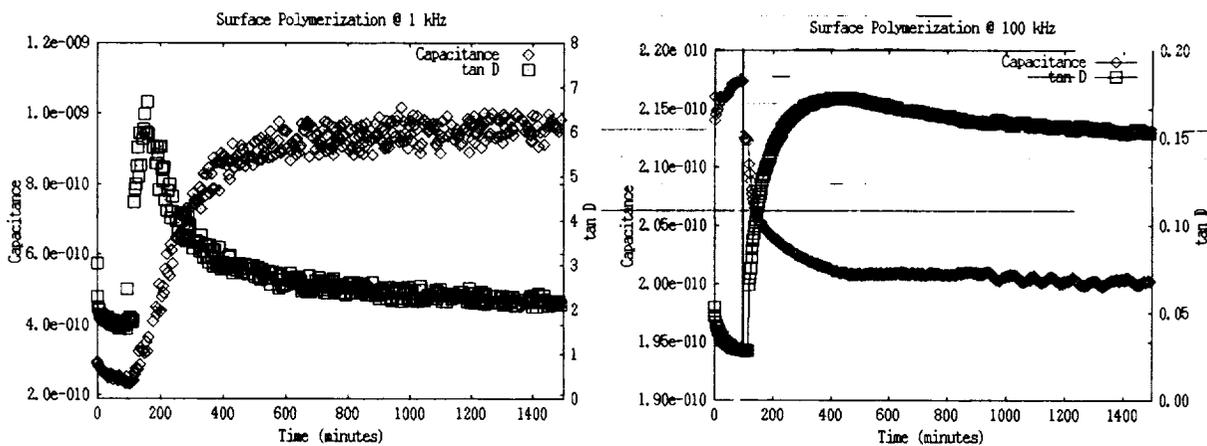
The response in the capacitance diminishes as the frequency increases and is completely diminished at 40 kHz. The peak in the dissipation factor at 200 minutes is not present at 4 kHz and higher. At 4 kHz the dissipation factor rises rapidly in the first 300 minutes, then peaks near 350 minutes and gradually decreases over time.

The peak observed in the capacitance of the bulk sample clearly indicates that the polymerization process has either decreased in rate or terminated. This decrease could be the result of the film growing on the surface decreasing the light intensity. There is a more gradual decrease in the capacitance for the surface measurement, which peaks 315 minutes after irradiation begins. This

decrease cannot be due to attenuation since the film should increase the capacitance as it continues to grow on the surface. The peak observed at 250 minutes in the dissipation factor at low frequencies is present in both the surface and bulk measurements. This suggest that the same process is active at both the surface and the bulk.

Conclusions

The in-situ dielectric spectra for the solution polymerization of polydiacetylene has been successfully measured. The results show a distinct difference between the response for the bulk solution and surface polymerization. It also shows a low frequency peak in the dissipation factor which is present in both the bulk and surface polymerizations. These features may prove to be significant indicators for important polymerization processes. Future studies will investigate the mechanisms responsible for this dielectric responses. This technique will eventually be used to monitor microgravity polymerizations and provide in-situ data on how microgravity affects solution polymerization.

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