FRONTAL POLYMERIZATION IN MICROGRAVITY: BUBBLE BEHAVIOR AND CONVECTION ON THE KC-135 AIRCRAFT

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Frontal polymerization is a mode of converting monomer into polymer via a localized exothermic reaction zone that propagates through the coupling of thermal diffusion and Arrhenius reaction kinetics. Frontal polymerization was discovered in Russia by Chechilo and Enikolopyan in 1972.[1] The macrokinetics and dynamics of frontal polymerization have been examined in detail[2] and applications for materials synthesis considered.[3]

Large temperature and concentration gradients that occur in the front lead to large density gradients. Figure 1 presents a schematic for a liquid monomer, usually a monoacrylate, being converted to a liquid (thermoplastic) polymer. The velocity can be controlled by the initiator concentration but is on the order of a cm/min.[2,4] If the liquid monomer is multifunctional, then a solid (thermoset) polymer is formed. Convection can occur with all types of monomers if the front propagates up a tube. Bowden et al. studied liquid/solid systems.[5] McCaughey et al. studied liquid polymer systems.[6] Descending fronts in thermoplastic systems are also susceptible to the Rayleigh-Taylor instability.[7]

I. Effective Interfacial Tension in Miscible Fluids

When two miscible fluids are placed in contact there exists a transient interfacial tension caused by differences in intermolecular forces. The theoretical basis goes back to an idea proposed in 1904, now called the Korteweg stress, in which a nonuniform concentration distribution can lead to stresses in a fluid.[8] Cahn and Hilliard developed the theory in 1958.[9] They proposed that the effective interfacial tension (EIT) should follow this relationship:

$$\sigma = k \int_\Omega | \nabla c |^2 d\xi$$

where C is the mole fraction of one component of a binary system, k is a constant with units of Newtons. If we consider a linear concentration gradient in one dimension, then we can write:

$$\sigma = k \frac{\Delta C^2}{\delta}$$

where δ is the length over which the concentration changes, and ΔC is the difference in composition.

Petitjeans measured the effective interfacial tension of glycerin and water, which are miscible in all proportions, using the spinning drop method and determined a value of 0.58 mN/m.[10] We have measured the dependence of the EIT and found it decreases with temperature. However, this is not true for hexyl acrylate/poly(hexyl acrylate), which increases with temperature.
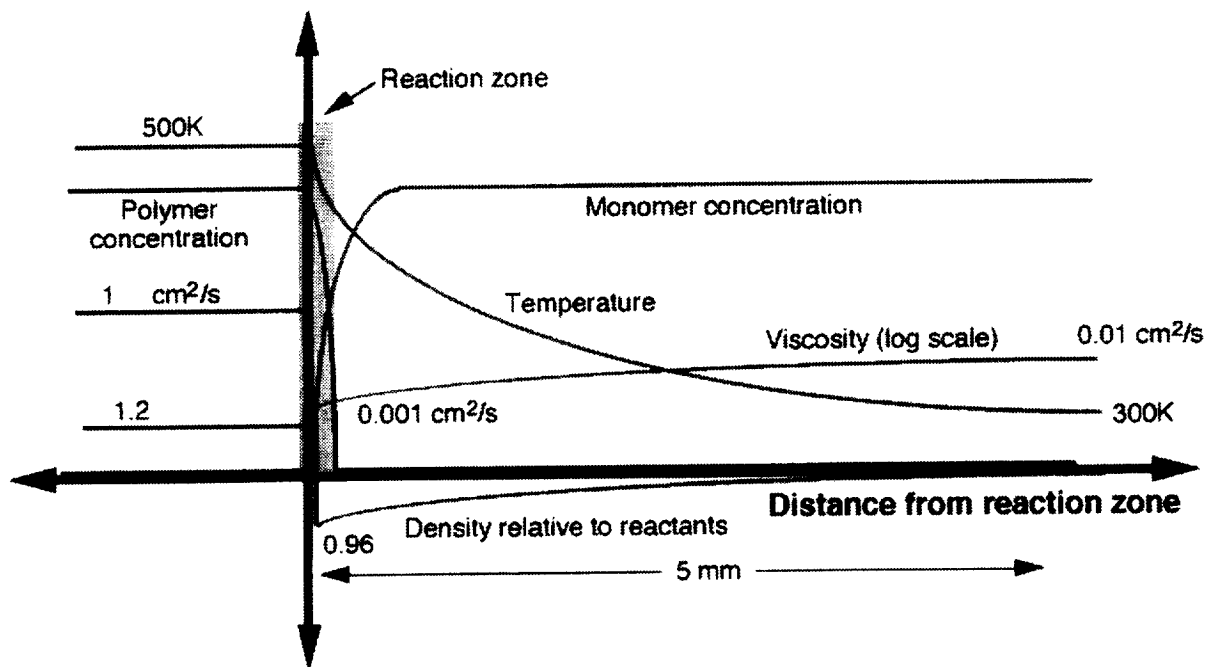

Figure 1. Schematic of a propagating polymerization front (liquid/liquid) showing approximate scales of variations in temperature, conversion, viscosity and density. Courtesy of Paul Ronney.

II. Effective-Interfacial-Tension Induced Convection (EITIC)

It is well known that temperature and/or concentration gradients perpendicular or parallel to a fluid/fluid interface can lead to convection.[11] Nonetheless, we know of no work on convection induced by effective interfacial tension gradients in miscible systems. Because of the large gradients produced in frontal polymerization, we propose that such convection could occur with a liquid monomer producing a liquid polymer. Specifically, measurements of the front width indicate that it decreases about 20% from the center of a 1.5 cm diameter tube to the walls, because of heat loss. We estimate the effective interfacial tension in the center of the tube to be 0.5 mN/m. At the wall it should be 0.4 mN/m.

Simulations for a model static system with the same gradient of interfacial tension with a single fluid indicates that flows would be has high as 20 cm/min for the monomer viscosity to 0.2 cm/min with 3 Stokes polymer.

We developed a numerical model based on Korteweg stresses induced by variations in the width of a sharp gradient and temperature gradients parallel to a uniform concentration gradient and demonstrated that convection can occur. The magnitude of the flow is comparable to that found in simulations with immiscible fluids but the flow exhibits a single vortex.

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Tubular Reactors: Frontal polymerization of thermoplastics is an excellent model of adiabatic tubular reactor polymerizations without flow. Tubular reactors are prone to fouling because of radial gradients in conversion and molecular weight.[12-14] Such reactors are complex because there are instabilities from the flow and from buoyancy-driven convection. Frontal polymerization is the static analog of an adiabatic tubular reactor. Our analysis indicates that EITIC should occur in the frontal polymerization of thermoplastics. Such a fluid flow would affect the conversion and molecular weight distribution of the polymer produced.

Effects of Bubbles and Foam Formation: Polymeric foams are ideal construction materials in low earth orbit because of their rigidity. Because the foam structures need stiffness without having to support their own weight, very large scale structures could be assembled. Moreover, foams could be very useful construction materials on the moon or Mars because of their inherent insulating capabilities and their ability to shield against micrometeorites. Experiments on the *Conquest 1* sounding rocket with butyl acrylate (thermoplastic) revealed an unusual bubble pattern in which nitrogen gas produced by the decomposition of the nitrile initiator formed a periodic structure.[7] For previous KC-135 experiments we reported that bubbles aggregated into large voids during weightlessness in the frontal polymerization of a thermoset.[15]

III. Experimental

Samples were flown aboard NASA's KC-135 aircraft. The parabolic flights afforded us approximately 20 seconds of low g (about 0.1 g) followed by a minute of 1 - 1.8 g. Tubes were 40 mm in diameter and equipped with a piston that moved in order to maintain isobaric conditions. _Hexyl acrylate and 1,6 hexane diol diacrylate were used as received from Aldrich. The initiator was a tricaprylmethyl ammonium persulfate (Aliquat 336 persulfate) that we synthesized.[16]

The thermoset foams consisted of 90% 1,6-hexane diol diacrylate (HDDA) with 10% 2-hydroxyethylmethacrylate (HEMA), which was added to slow the front velocity so that multiple parabolas could be seen in the same sample. A 10% Aliquat persulfate (tetraalkylammonium persulfate) solution was added to the monomer mixture as a bubble free initiator that will form free radicals. The blowing agent solution was made up of 5% Aliquat 336 and 95% distilled water. The Aliquat was added as a surfactant to allow the water to be dispersed in the organic monomer solution.

Reactions were initiated by heating the outside of the tube (for foam experiments) or by a nichrome wire directly in contact with the hexyl acrylate. Glycerin and water were studied by injecting one fluid (containing a dye) into the other in an apparatus that was free floated, allowing approximately 5 seconds of weightlessness.

IV. Results and Discussion

Attempts to observe convection in mg: With the frontal polymerization of hexyl acrylate we attempted to observe convection caused by the supposed gradient of effective interfacial tension. It was not possible to initiate the front and observe propagation in 20 seconds. Also, bubbles appeared from dissolved air. Figure 2 shows two images separated by a few seconds demonstrating how g jitter mixed the system. Even in high g the front sustained itself although the Rayleigh-Taylor instability was apparent (Figure 2). Molten polymer circulated above the front because of

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heat loss, which caused a vertical gradient density. Polymer also sank from the front because it is more dense even when hot. Although the front would then propagate without any apparent convection during the next low g period, the convection reduced any radial gradient that would have been present and could have induced a fluid flow.

Thermoset Foams: As predicted, the bubble size did increase as the level of gravity decreased, but there was an overlap of the bubbles produced in microgravity into the region produced in 1.8 g. This overlap of regions eliminated our ability to measure the density of the foams produced.
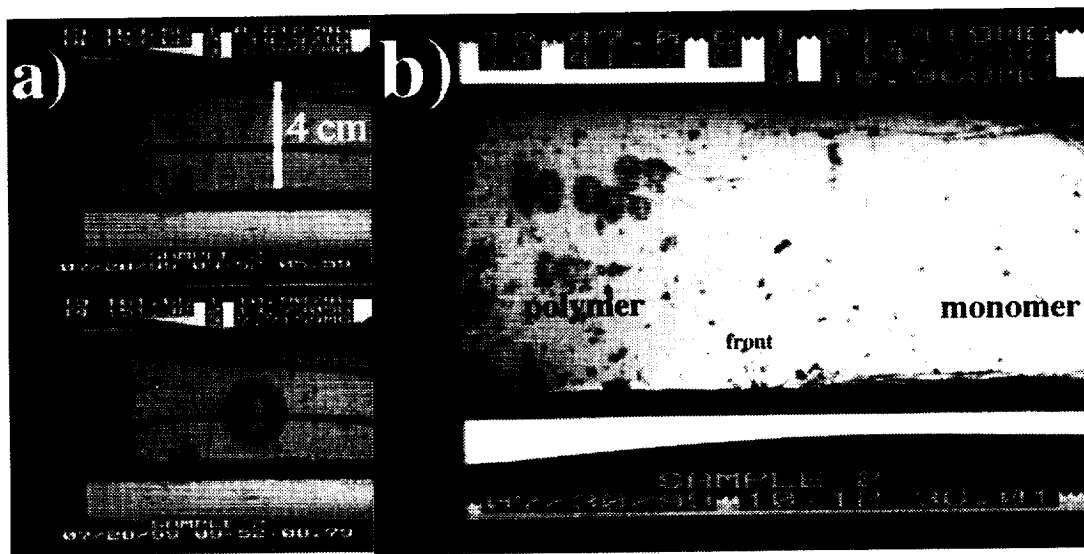

Figure 2. a) Two images of a hexyl acrylate polymerization front in the low g phase of the parabola. Notice how the bubble has moved to the right (down). b) The Rayleigh-Taylor instability in 2 g. "Down" is toward the right.
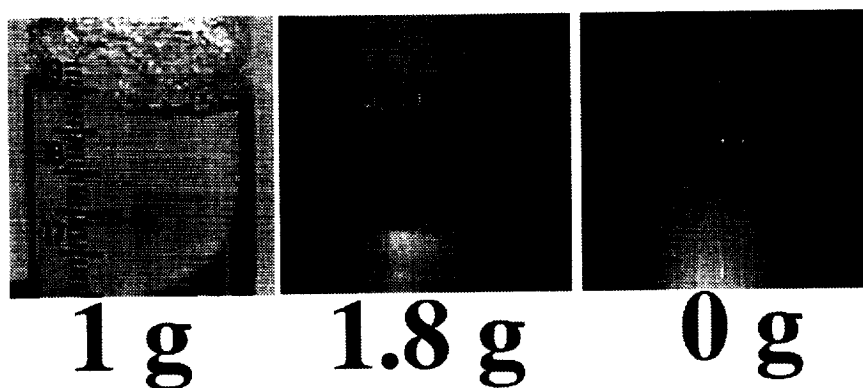

Figure 3. Bubbles in thermoset foams. Tubes are 2 cm in diameter.

V. Observations of Glycerin and Water in Low g

A question that arises if an effective interfacial tension exists is whether a drop of a miscible fluid spontaneously becomes spherical or if a jet spontaneously breaks into drops. We studied water injected into glycerin and glycerin injected into water in low g on the KC-135 aircraft. We free floated the apparatus to achieve quiescent conditions but only for a few seconds. Figure 4 shows how a drop of water does not become spherical during the short low g period. A stream of glycerin in water does not break into drops as could be expected from the Rayleigh instability for immiscible fluids. From Levich, we can estimate the time required for droplet breakup:[17]

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$$\tau = \frac{5 * \text{radius} * \mu}{\sigma} = \frac{5(0.001m * 1Pa* s)}{0.001mN/m} = 5s$$

The time scale is somewhat longer than the observation peroid allowed but no constriction of the stream was observed. It may be that the g jitter and fluid flow during injection perturbed the concentration gradient and reduced the EIT.

We performed another study to test if EITIC could be induced by a temperature gradient along a miscible interface. Water was carefully layered onto glcyerin. A light bulb was situated at the interface, which could heat the surrounding fluid 10°C in 2 seconds (Figure 5b). The experiment was free floated just after the heater was started. No fluid motion along the interface could be detected in the glycerin. Glycerin is so viscous that any flow would be very slow. Therefore, we diluted the glycerin with water, which would reduce the EIT but more rapidly decrease the viscosity. Unfortunately, the slightest bump to the apparatus in free float disrupted the interface.

VI. Conclusions

Experiments under weightlessness show clearly that frontal polymerization with bubbles produces foams with different bubble sizes in weightlessness. However, the bubbles produced during the high g phase affect the bubbles during the low g making it impossible to determine what the behavior would be if the front propagated only under low gravity.

Numerical simulations indicate that an effective-interfacial-tension induced convection can occur because of concentration and temperature gradients between a polymer and its miscible monomer. Because of g jitter, it was not possible to determine if the predicted effective interfacial tension gradient in a front causes convection in a front with a liquid monomer producing a liquid polymer. Model experiments with glycerin and water were inconclusive.

To determine how effective-interfacial-tension induced convection could affect polymer processing requires low periods of higher quality weightlessness.

VII. Acknowledgments

REFERENCES

1. Chechilo, N. M.; Khvilivitskii, R. J.; Enikolopyan, N. S. *Dokl. Akad. Nauk SSSR* 1972, *204*, 1180-1181.
2. Pojman, J. A.; Ilyashenko, V. M.; Khan, A. M. *J. Chem. Soc. Faraday Trans.* 1996, *92*, 2825-2837.
3. Khan, A. M.; Pojman, J. A. *Trends Polym. Sci. (Cambridge, U.K.)* 1996, *4*, 253-257.
4. Goldfeder, P. M.; Volpert, V. A.; Ilyashenko, V. M.; Khan, A. M.; Pojman, J. A.; Solovyov, S. E. *J. Phys. Chem. B* 1997, *101*, 3474-3482.
5. Bowden, G.; Garbey, M.; Ilyashenko, V. M.; Pojman, J. A.; Solovyov, S.; Taik, A.; Volpert, V. *J. Phys. Chem. B* 1997, *101*, 678-686.

6. McCaughey, B.; Pojman, J. A.; Simmons, C.; Volpert, V. A. *Chaos* 1998, *8*, 520-529.
7. Pojman, J. A.; Khan, A. M.; Mathias, L. J. *Microgravity Sci. Technol.* 1997, *X*, 36-40.
8. Korteweg, D. J. *Archives Neerl. Sci. Exacts. Nat.* 1904, *6*, 1.
9. Cahn, J. W.; Hilliard, J. E. *J. Chem. Phys.* 1958, *28*, 258-267.
10. Petitjeans, P. *C.R. Acad. Sci. Paris* 1996, *322*, 673-679.
11. Ostrach, S. *Annu. Rev. Fluid Mech.* 1982, *14*, 313-345.
12. Cunningham, M. F.; O'Driscoll, K. F.; Mahabadi, H. K. *Can. J. Chem. Eng.* 1991, *69*, 630-638.
13. Cunningham, M. F.; O'Driscoll, K. F.; Mahabadi, H. K. *Polym. Reaction Eng.* 1992, *1*, 229-244.
14. Cunningham, M. F.; O'Driscoll, K. F.; Mahabadi, H. K. *Polym. Reaction Eng.* 1992, *1*, 245-288.
15. Pojman, J. A. *Frontal Polymerization in Microgravity, AIAA 98-0813*; AIAA: Reno, NV, 1998.
16. Chekanov, Y.; Pojman, J. A.; Rasmussen, J. K. *Polym. Prepr. (Am Chem. Soc. Div. Polym. Chem.)* 1998, *39*, 465-467.
17. Levich, V. G. *Physicochemical Hydrodynamics*; Prentice Hall:, 1962.
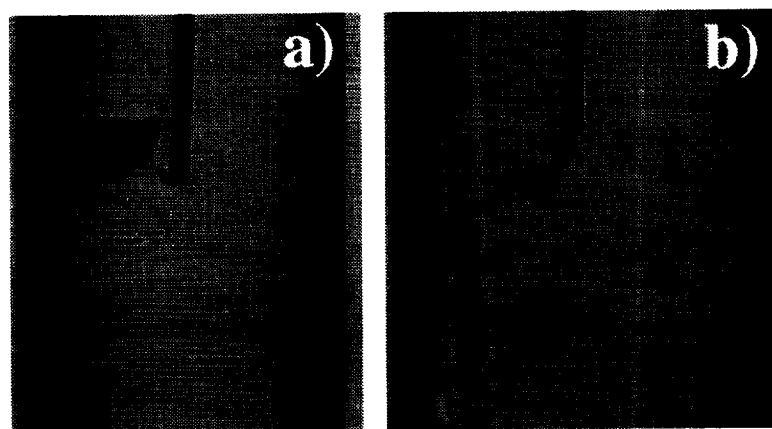
Figure 4. a) Water injected into glycerin in low g. b) Glycerin injected into water in low g. Tube diameter of 2.2 cm.
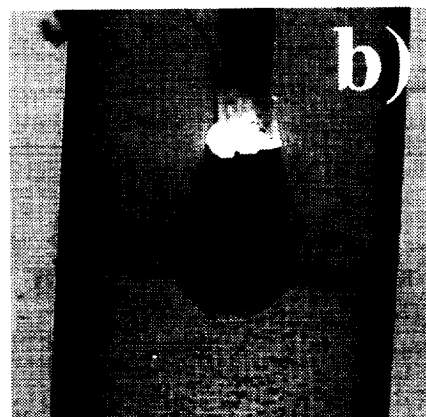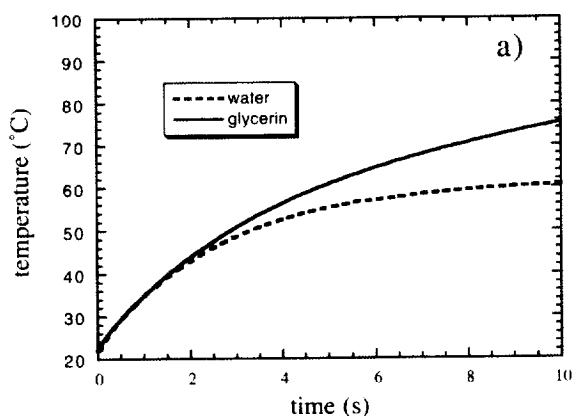

Figure 5. The time dependence of the heater. Glycerin under water in a 2.2 cm diameter tube.