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Suppressing Convective Instabilities in Propagating Fronts by Tube Rotation

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Received: September 5, 1995; In Final Form: November 7, 1995[⊗]

Density gradients caused by thermal and solutal gradients often cause double-diffusive and/or Taylor instabilities in propagating fronts. These instabilities manifest themselves as “fingering” that can affect the front shape and velocity and, in extreme cases, destroy the front. This is especially a problem with propagating fronts of polymerization when a monomer is used that does not produce a cross-linked polymer. We have found that it is possible to suppress the fingering by rotating the tube around the long axis of the tube. With the chlorate–sulfite system and methacrylic acid polymerization system, we found that the front velocities exhibited a fourth-order dependence on the rotational frequency, and the front shapes were parabolic. The amplitudes of the deviation of the fronts from a planar front exhibited a second-order dependence on the rotational frequency but not exactly as predicted from the hydrostatic analysis of a rotating fluid.

Introduction

Propagating fronts of exothermic polymerization reactions were first discovered at the Institute of Chemical Physics in Chernogolovka, Russia, by Chechilo and Enikolopyan in 1972.¹ Having observed that fronts with methyl methacrylate were susceptible to a Rayleigh–Taylor instability (higher density polymer overlying less dense monomer) unless very high pressure was applied, they studied fronts at ambient pressure with a diacrylate that forms a solid product.²

We independently rediscovered the existence of traveling fronts in solutions of thermal free-radical initiators in a variety of neat monomers at ambient pressure using liquid monomers that form polymers with melting points exceeding the reaction temperature of the front,^{3,4} and we discovered the existence of fronts with a solid monomer.⁵ Unstable modes of propagation have been found under some conditions.⁶

We expect that the propagating front approach will ultimately have three benefits over traditional methods of polymer synthesis: (1) reduced energy costs, (2) reduced waste production, and (3) unique morphologies. A unique feature of propagating fronts is their ability to convert rapidly and uniformly monomer to polymer. Performing an adiabatic polymerization of a neat monomer is difficult at best and dangerous at worst. But it can be advantageous because the heat of the reaction is used to increase the rate of reaction, making for very rapid conversion. Also, the lack of solvent eliminates the need to separate the polymer from the solvent, which requires energy and can have environmental ramifications. Recently, we demonstrated that a thermochromic composite could be prepared more effectively via frontal polymerization than with traditional homogeneous methods because the rapid reaction in the front prevented phase separation and sedimentation.^{7,8}

The picture is not quite so rosy because of a major interference caused by convection. In experiments with liquid monomers such as methacrylic acid, a special case of double-diffusive convection, so-called “fingering”, was observed under the descending front.⁴ The fingering affected the front velocity and left a hole in the polymer product. The appearance of fingering

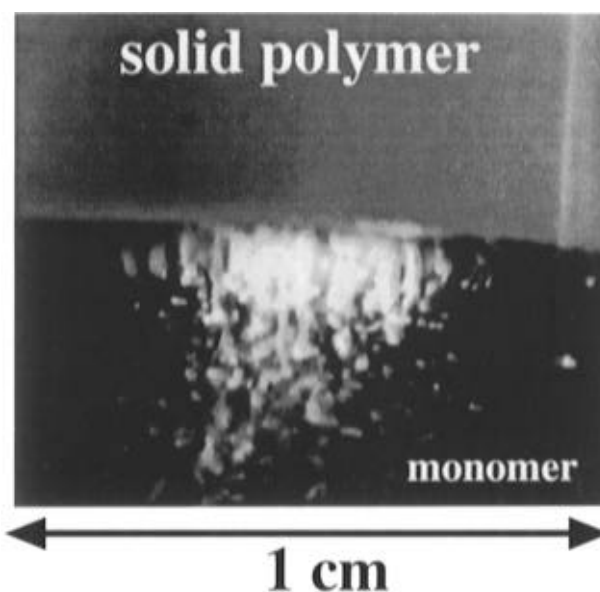


Figure 1. Fingering observed during the propagation of methacrylic acid polymerization front with 1% w/v benzoyl peroxide as the initiator.

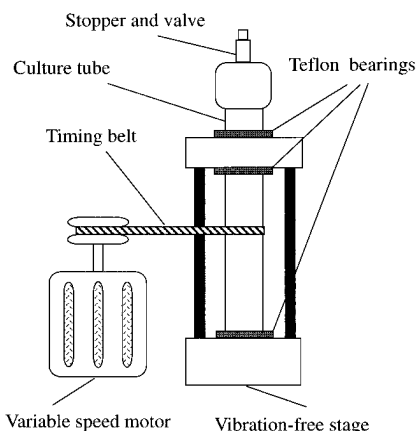


Figure 2. Schematic of the device used to rotate the tubes.

was sensitive to the initiator concentration and initial temperature. Figure 1 shows fingering in a methacrylic acid front. Using butyl acrylate, which forms a molten polymer at the front

[⊗] Abstract published in *Advance ACS Abstracts*, January 15, 1996.

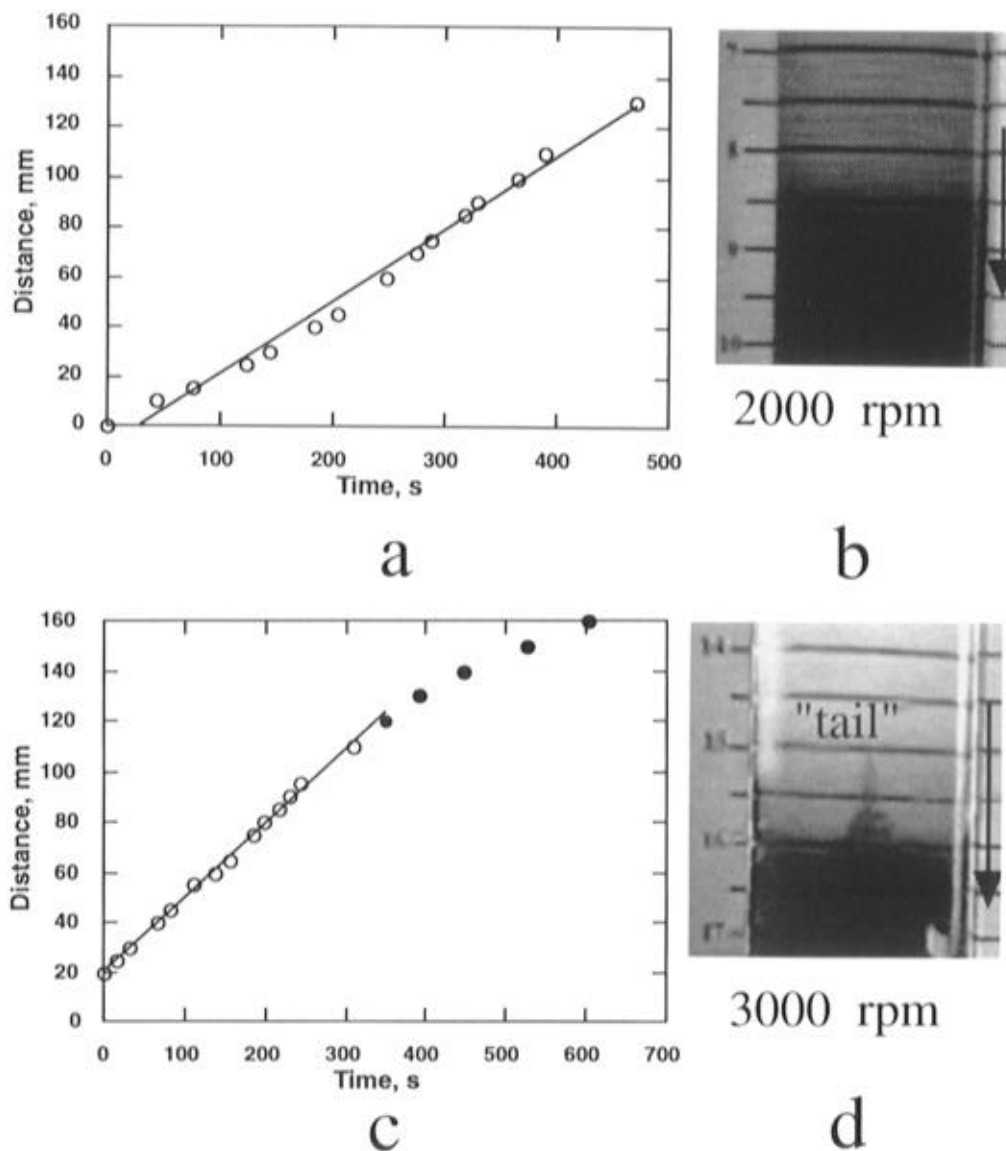


Figure 3. Position versus time curve of the chlorate–sulfite front propagation (a) and the wave shape (b) at 2000 rpm frequency; (c, d) at 3000 rpm frequency, respectively.

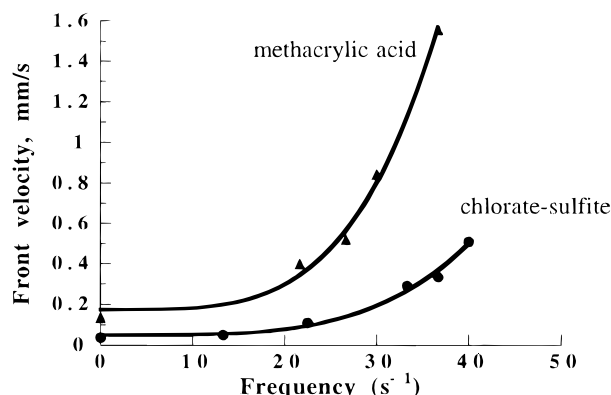


Figure 4. Effect of the rotation speed on the velocity of the polymerization front in the chlorate–sulfite system (●) and the methacrylic acid–benzoyl peroxide system (▲).

temperature, the front completely collapses from a Rayleigh–Taylor instability.

There are several possibilities to suppress the phenomenon: changing the initiator concentration or increasing the viscosity of the liquid phase by adding a gel forming material. These methods have serious effects on the overall nature of the reaction front and sometimes do not result in a proper propagation

because the front can be slowed down or extinguished. Further, the product is no longer homogeneous but becomes a composite. For any possible future applications of the frontal polymerization method it is important to control and/or suppress the double-diffusive and Taylor instabilities. Therefore, we sought other methods.

Schulze and Davis have shown that circular tube motion can suppress morphological instabilities in directional solidification.⁹ More directly, relevant work has been done that shows rotation can have a stabilizing effect on double-diffusive convection.^{10–12} None of these latter works considered the effects on convection in a propagating front. However, these theoretical results did inspire us to determine whether rotating the tube could suppress convective fingering with aqueous chemical waves and polymerization fronts.

The conditions for double-diffusive convection in propagating fronts have been studied for several systems.^{13–19} The chlorate–sulfite system is a simple system to study that produces pronounced fingering.¹⁸ We have chosen it as a model system to determine the effect of tube rotation on front velocity and front stability. We have then applied the technique to propagating fronts of methacrylic acid polymerization and of butyl acrylate polymerization.

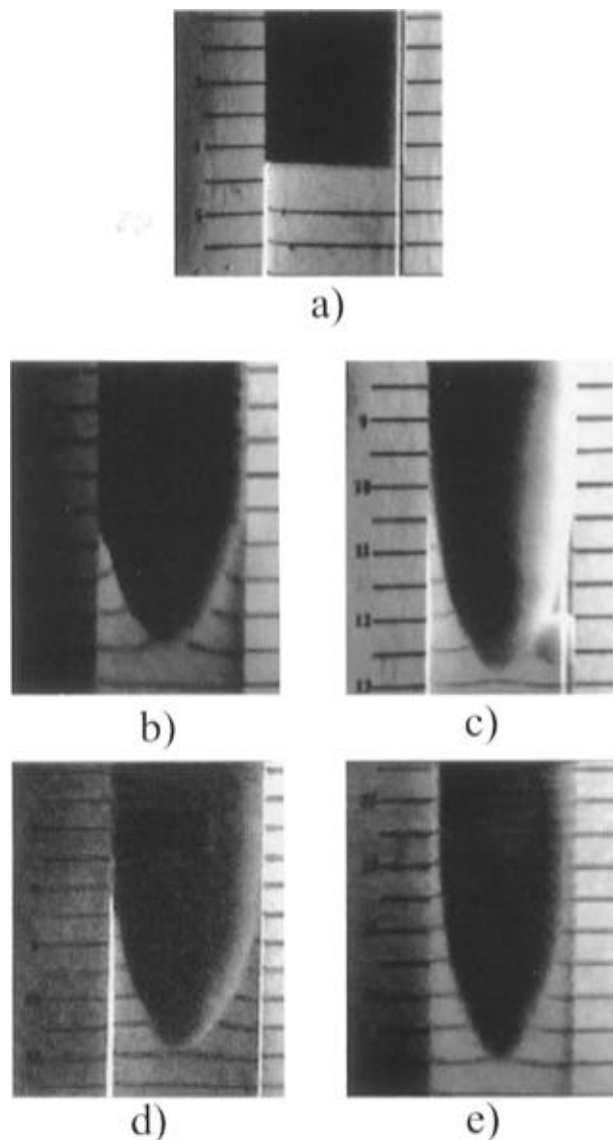


Figure 5. Front shapes at several speeds of rotation during the propagation of the polymerization front in the methacrylic acid–benzoyl peroxide system at (a) 0, (b) 1300, (c) 1600, (d) 1800, and (e) 3200 rpm frequency. In (c) to the right of the edge of the parabolic front a small drop of polymerizing mixture can be seen falling and being stabilized at the edge of the tube. Later it was engulfed by the front and uniform propagation ensued.

Experimental Section

Chemicals and Apparatus. For aqueous phase experiments reactant solutions were prepared with analytical grade chemicals that were used as received: Na_2SO_3 and H_2SO_4 from Fisher; KClO_3 and bromophenol blue from Aldrich; and deionized water. The stock solution of bromophenol blue was 15% w/v.

Wave experiments were carried out using a KIMAX culture tube (25×250 mm, inner diameter 22 mm). The culture tube was filled with 90 mL of the reaction mixture prepared from appropriate stock solutions of the reactants. The initial concentrations in the tube before initiating the reaction were Na_2SO_3 (0.832 M): H_2SO_4 (0.115 M): KClO_3 (0.325 M). A total of 5–10 drops of indicator solution was added. The tube then was sealed with a SUBA SEAL septum stopper with minimal air gap above the solution. This gap was later filled by injecting approximately 1 mL of 2.3 M H_2SO_4 with needle and syringe to initiate the wave. The tube then was placed into the holes of the Teflon bearings of the device shown in Figure 2. Bearings were lubricated with a few drops of light mineral oil.

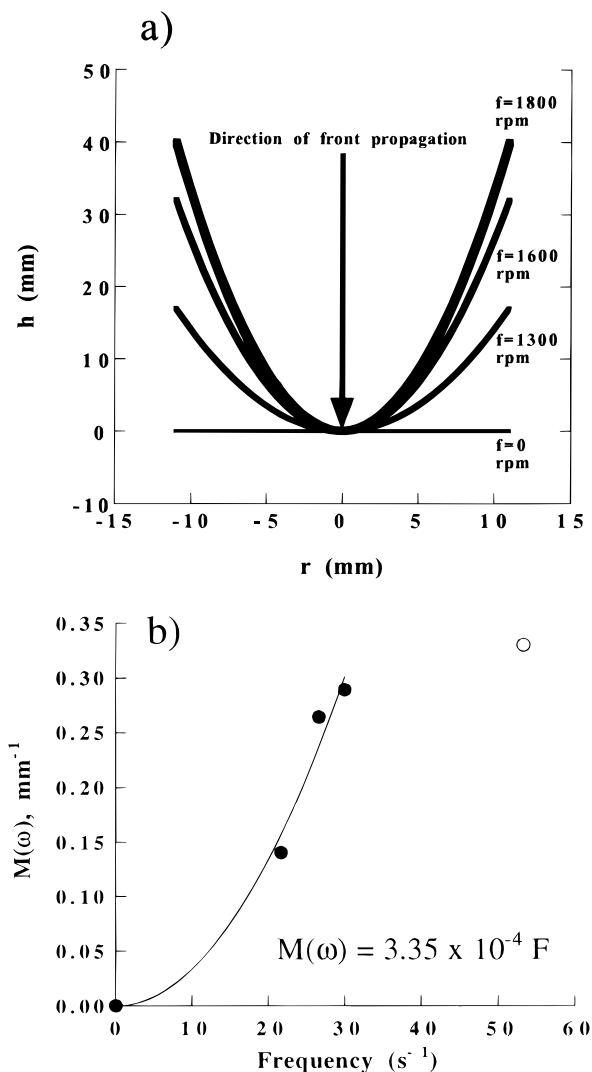


Figure 6. (a) Front shapes evaluated from the images captured during experiments. (b) Shape coefficient as a function of the frequency of rotation.

A 110 V “60” W motor with a variable speed control between 500 and 7500 rpm rotated the tube via a pulley and belt, which was simply a rubber ring replaced after each experiment because of mechanical damage. The frequency of the rotation was determined using a stroboscope (Digistrobe, AMETEK) with ± 20 rpm accuracy.

For poly(methacrylic acid) front experiments methacrylic acid and benzoyl peroxide (BPO) came from Aldrich. BPO (0.5% m/v) was dissolved in degassed methacrylic acid. A 90 mL sample of the solution was put in the culture tube, and the front was initiated by adding both 0.5 mL of both pure *N,N*-dimethylaniline and a solution of 1.0% m/v BPO dissolved in methacrylic acid. The front was allowed to propagate down at least 4 cm to obtain solid poly(methacrylic acid) on the top of the solution. Then the tube was sealed with a thermoplastic sealant (“glue gun” glue) to prevent the liquid from escaping through the porous poly(methacrylic acid). The rotation of the tube was begun only after perfect sealing.

Imaging. Visible images from a Hitachi solid state color camera equipped with a Cosmimar zoom lens were digitized with a Data Translation board on a Macintosh Quadra 800. Analysis of captured images was performed with Image 1.41 (from NIH). The wave shape evaluation in the case of methacrylic acid polymerization fronts required image enhancement and edge detection using Sobel filtering.²⁰

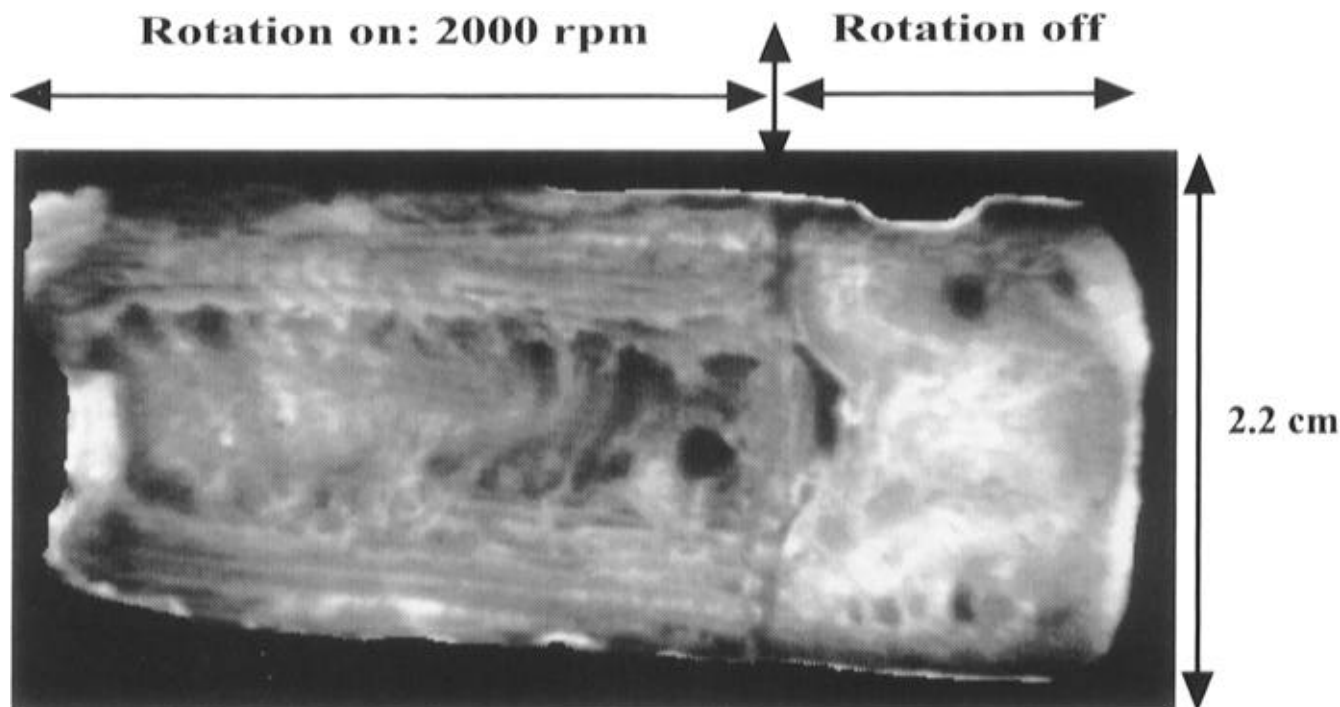


Figure 7. Effect of changing the frequency of rotation from 0 to 2000 rpm on the cross-sectional morphology of a poly(methacrylic acid) sample.

Results and Discussion

Wave velocities were determined in all experiments from the distance–time plots. When the frequency of rotation was 0 or low, these curves were straight lines, and the slopes provided the wave velocity. In simple cases the slope was constant along the entire tube (Figure 3a). During experiments on the chlorate–sulfite system we observed a strange phenomenon above 2000 rpm, which caused deviation in the later stage of the distance–time curve (Figure 3c). During propagation with slow rotation rates the wave shape was relatively simple and fingering was suppressed (Figure 3b). Thus, our original goal was accomplished. With high rotation frequency (>2500 rpm) the fluid flow was reflected from the bottom of the rotating tube. A small “tail” in the front can be seen in Figure 3d.

We attempted to extend the concept to butyl acrylate fronts, which are so susceptible to fingering that stable fronts will not propagate unless a thickening agent is added. Unfortunately, this method did not work. We were unable to initiate a front while rotating the tube without fingering spreading the heat throughout the solution, causing a homogeneous and vigorous reaction. At least part of the problem was caused by vibrations.

Figure 4a presents the chlorate–sulfite front velocity dependence on the rotation frequency. The same dependence was found for the methacrylic acid polymerization front under spinning conditions (Figure 4b). In both cases, a function of the following form was successfully fit to the data:

$$\text{velocity} = A + B\omega^4 \quad (1)$$

The shape of the polymerization front was also studied. As shown in Figure 5, the originally flat front (with fingering that is difficult to see in the image) turned to a parabolic shape even with slow rotation. The curvature of the parabola increased with higher rotation rates. We measured the shape of the fronts and found that they were described exactly with parabolic functions. Putting the minimum of the parabola at the origin, an equation can be determined as

$$h(r) = Mr^2 \quad (2)$$

where $h(r)$ is the height of the front at position r measured with respect to the plane tangent to the tip of the front (see Figure 6a) and M is a constant at a fixed rotation rate throughout propagation, except at the end of the tube (see below). Figure 6a shows the wave shapes as exact parabolic curves as a function of the rotational frequency. The parameter M has a second-order dependence on the frequency (Figure 6b), which suggests that the front shape is a direct function of the centrifugal force. Figure 6b has a data point at 3200 rpm that does not fit the curve. As in the case of the chlorate–sulfite system, this deviation is related to the end effect observed at higher frequencies and probably also to the vibration occurring in the range of the frequency 2500–3300 rpm.

A classical problem in hydrostatics is the shape of a liquid/air interface in a rotating cylinder.²¹ The result of balancing the centrifugal and gravitational forces on the liquid is this expression for the height of the liquid:

$$h(r) = \omega^2 r^2 / 8\pi^2 g \quad (3)$$

Comparing eq 2 with eq 3, we can see that $M(\omega)$ in (2) is simply $\omega^2 / 8\pi^2 g$ (with ω in s^{-1}) and that the maximum deviation from planarity should indeed be proportional to the second power of the rotational frequency! A second-order fit of M versus ω yields of a factor of $3.3 \times 10^{-4} \text{ s}^2 \text{ mm}^{-1}$. From eq 3 we calculate $(8\pi^2 g)^{-1}$ with a value of $1.3 \times 10^{-6} \text{ s}^2 \text{ mm}^{-1}$. Thus, it is reasonable to conclude that the front shape is a function of the centrifugal force but not due to a simple balance between gravity and that force. The front elongates more as a function of the rotational frequency than predicted, probably reflecting the fact that the interface is not stationary but propagating and the effects of convection caused by the radial temperature gradients.

Because the chlorate–sulfite front appears as a light colored region propagating into dark colored solution, we were unable to measure the front shape accurately. It may be possible to use other indicators. However, it appears to be parabolic.

Vibration is a problem with the experimental setup, and we point out that even at low rotation frequencies it can cause minor

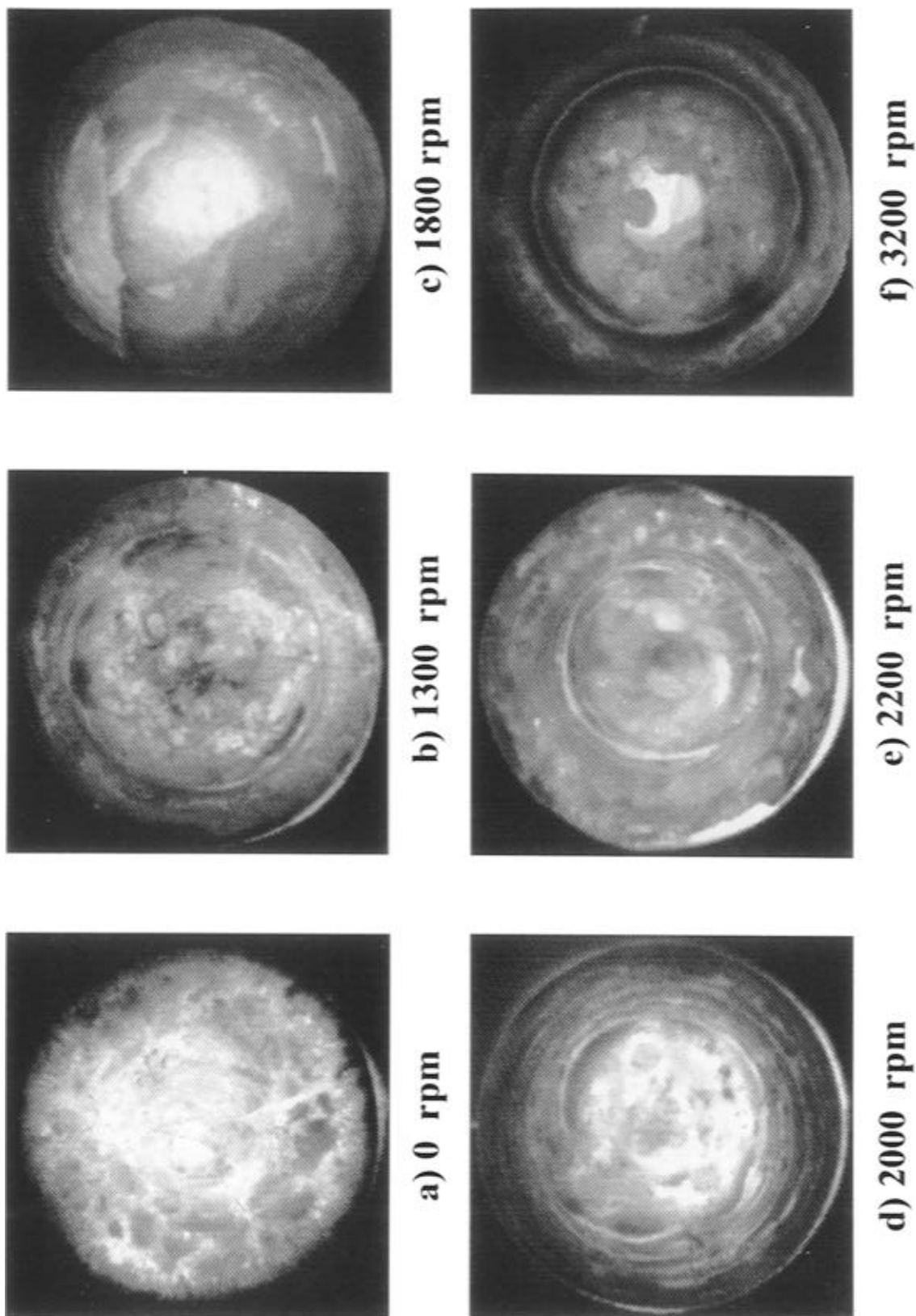


Figure 8. Effect of frequency of rotation on the morphology of cross sections of poly(methacrylic acid) samples.

disturbances. In Figure 5c to the right of the edge of the parabolic front a small drop of polymerizing mixture can be seen falling and being stabilized at the edge of the tube. Later it was engulfed by the front and uniform propagation ensued. However, at lower frequencies we did not observe any serious disturbing effect on the velocity or shape.

The frequency of rotation has a significant effect on the morphology of the solid product. In Figure 7 the effect of the rotation can be observed. When there is no rotation, the material is transparent and lacks any macroscopic pattern. After switching on rotation at a rate of 2000 rpm, the morphology dramatically changes; concentric rings of translucent polymer appear in the cross section (Figure 8d). The center of the sample is less structured than the perimeter region. Briskman et al. have studied the effect of rotation on polymer gel formation and also found a radial dependence of the structure.²²

The systematic change can be understood by Figure 8a–f, where cross sections show increasing order and number of rings from 0 to 2000 rpm. First (at 1300 rpm), the glassy structure begins to shrink and a few concentric structures appear. At 1800 rpm the glassy part is centered close to the axis of the tube, and many small concentric rings can be observed. At 2000 rpm the structures are sharper, and just a small portion of the cross section is glassy. At 2200 rpm vibration begins to disturb the organized structure formation, which obviously continues at 3200 rpm, where a hole can be seen at the center. At the same time the glassy portion of the sample begins to increase again. What happens at higher frequencies is unknown because we do not know how much vibration affects the product morphology. The speed and wave shape evaluation indicate that to yield reliable results in the higher frequency region we need to find better conditions to stabilize the rotation, which is difficult with commercial tubes and our simple belt drive.

Conclusions

Our results show that convective instabilities can be suppressed by rotating a tube around its long axis. This method works for purely liquid phase as well liquid–solid phase systems. The dependence of the wave velocity in both cases was found to be a fourth-order function of the rotational frequency, which suggests a second-order dependence on the centrifugal force. The wave shape is a parabola and a second-order function of the rotation rate as in the classical case of a rotating fluid. The exact dependence on the frequency is 2 orders of magnitude greater than the hydrostatic model predicts.

Unfortunately, this technique did not work with a molten polymer front. We hope that an improved device may make this technique a general one for the study of propagating polymerization fronts.

The method could have synthetic use if the relationship between the structured product and the molecular weight distribution (and conversion) within the parts of the anisotropic samples becomes clearly understood.

Acknowledgment. This work was supported by the U.S.–Hungarian Science and Technology Joint Fund (Grant J.F. 247/92a), the National Scientific Research Fund of Hungary (OTKA Grants F-4024 and F-016166), the Ministry of Education of the Hungarian Government (MKM Grant 9/94), and the Air Force Office of Scientific Research. We thank Marc Garbey for suggesting the comparison to the classical hydrostatic problem and Ray Folse for helpful discussions.

References and Notes

- (1) Chechilo, N. M.; Khvilivitskii, R. J.; Enikolopyan, N. S. *Dokl. Akad. Nauk SSSR* **1972**, *204*, 1180–1181.
- (2) Chechilo, N. M.; Enikolopyan, N. S. *Dokl. Phys. Chem.* **1974**, *214*, 174–176.
- (3) Pojman, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 6284–6286.
- (4) Pojman, J. A.; Craven, R.; Khan, A.; West, W. *J. Phys. Chem.* **1992**, *96*, 7466–7472.
- (5) Pojman, J. A.; Nagy, I. P.; Salter, C. *J. Am. Chem. Soc.* **1993**, *115*, 11044–11045.
- (6) Pojman, J. A.; Ilyashenko, V. M.; Khan, A. M. *Physica D* **1995**, *84*, 260–268.
- (7) Nagy, I. P.; Sike, L.; Pojman, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 3611–3612.
- (8) Nagy, I. P.; Sike, L.; Pojman, J. A. *Adv. Mater.*, in press.
- (9) Schulze, T. P.; Davis, S. H. *J. Cryst. Growth* **1995**, *149*, 253–365.
- (10) Antoranz, J. C.; Velarde, M. G. *Phys. Fluids* **1979**, *22*, 1038–1043.
- (11) Guo, J.; Kaloni, P. N. *J. Math. Anal. Appl.* **1995**, *190*, 373–390.
- (12) Toole, J. M.; Georgi, D. T. *Prog. Oceanog.* **1981**, *10*, 123–145.
- (13) Pojman, J. A.; Epstein, I. R.; McManus, T.; Showalter, K. *J. Phys. Chem.* **1991**, *95*, 1299–1306.
- (14) Pojman, J. A.; Epstein, I. R. *J. Phys. Chem.* **1990**, *94*, 4966–4972.
- (15) Pojman, J. A.; Epstein, I. R.; Nagy, I. *J. Phys. Chem.* **1991**, *95*, 1306–1311.
- (16) Keresztessy, A.; Nagy, I. P.; Bazsa, G.; Pojman, J. A. *J. Phys. Chem.* **1995**, *99*, 5379–5384.
- (17) Nagy, I. P.; Keresztessy, A.; Pojman, J. A.; Bazsa, G.; Noszticzius, Z. *J. Phys. Chem.* **1994**, *98*, 6030–6037.
- (18) Nagy, I. P.; Pojman, J. A. *J. Phys. Chem.* **1993**, *97*, 3443–3449.
- (19) Nagy, I. P.; Pojman, J. A. *Chem. Phys. Lett.* **1992**, *200*, 147–152.
- (20) Russ, J. C. *The Image Processing Handbook*; CRC Press: Boca Raton, FL, 1995.
- (21) Debler, W. *Fluid Mechanics Fundamentals*; Prentice-Hall: Englewood Cliffs, NJ, 1990.
- (22) Briskman, V. A.; Kostarev, K. G.; Lyubimova, T. P. In *Materials Processing in High Gravity*; Regel, L. L., Ed.; Plenum: New York, 1994; pp 185–191.

JP9526004