



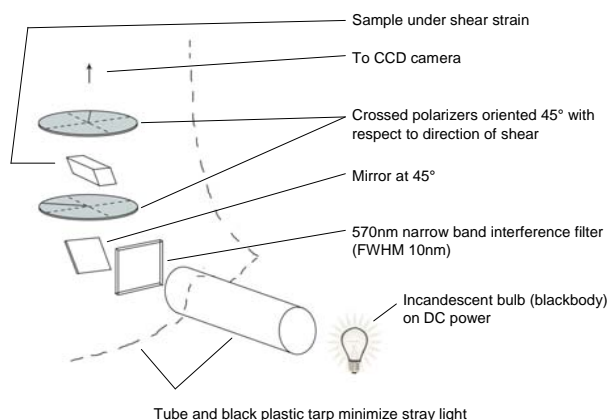
TREND
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Flow Birefringence of Aqueous Polyacrylamide Solutions

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Background: Birefringent materials contain anisotropies such that the index of refraction along the axis of anisotropy varies from that of the axis orthogonal to it. Many polymeric fluids exhibit birefringence under shear stress due to anisotropies introduced as the polymer chains become aligned with the direction of flow. Birefringence has been observed anecdotally in aqueous solutions of polyacrylamide (PAAm), and this study is an effort to reproduce this effect under controlled shear.

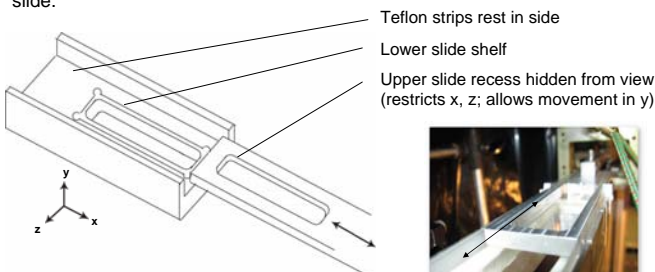
1. Basic Experimental Setup



2. Primary Setup: Oscillatory Shear

The shearing unit consisted of a stationary base with a shelf and window fitted for a standard microscope slide. A sliding top with a similar recess was connected to a shaker. Strips of Teflon between these two slides determined the gap width and aided in the motion of the top slide.

In this setup, birefringence would appear as a cyclical change in the amount of light transmitted through the sample over the course of the oscillation of the top slide.



Results:

- Tested aqueous solutions of PAAm ($M_w = 18$ Mg/mol) with concentrations of 2.0%, 1.0%, 0.5%, 0.1%, 0.01%, 50ppm, and 5ppm, primarily with a gap width of $.005'' \pm .002$ up to a shear rate of $\sim 8000s^{-1}$

→ No birefringence observed

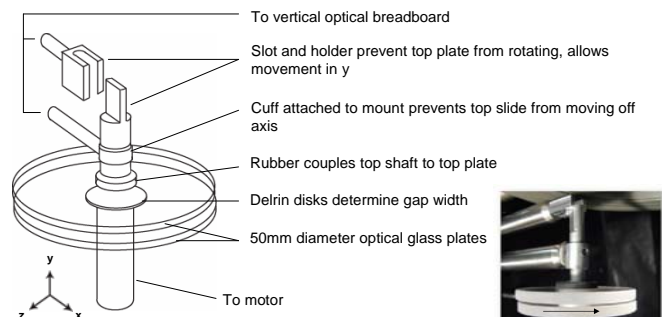
- Multiple modifications were made to the setup and method in the attempt to produce birefringence, avoid unwanted effects (bubbles between slides, etc), and increase the path length through fluid layer.

3. Secondary Setup: Continuous Shear

Thinking that oscillatory shear might not allow the polymer chains to elongate enough for the fluid to display birefringence, a setup which employed continuous shear was constructed. This consisted of a bottom rotating plate and a top stationary plate which was free to move in the y direction only. The gap width was determined by Delrin cylinders affixed to the bottom plate by double stick tape (added $.005''$ to gap width).

In this case, birefringence would:

- appear as a bright line along the radius of the plates with the orientation determined by the orientation of the crossed polarizers
- become more pronounced toward the plate edges (increasing shear rate as distance from rotation axis increases)
- fade as polymer relaxes when rotation is stopped



Results:

- Tested aqueous solutions of PAAm with concentrations of 2.0%, 1.0%, 0.5%, 0.1%, 0.01%, 50ppm for gap widths of $.155''$, $.115''$, $.080''$, $.060''$, and $.040'' \pm .002$ (max shear at minimum gap width $\sim 900s^{-1}$)

→ No birefringence observed

- Many instabilities and classic Non-Newtonian behaviors, particularly for concentrations of PAAm $> .5\%$ (finger-like projections, clumping around rotation axis/pushing up top plate, etc)

4. Testing with poly(ethylene oxide) (PEO)

To ascertain whether birefringence would be observed for a known birefringent polymer with these setups, each was tested with 1.0%, 0.75% and 0.5% concentration aqueous solutions of PEO. Several birefringence studies of PEO under shear can be found in the literature (see for example Frank and Mackley, 1976).

For our setups, no strong birefringence was observed (some of the data suggested very weak birefringence). However, the molecular weight (4Mg/mol) was fairly low for studies of this nature, and flow instabilities in the rotating plate geometry made it difficult to test higher concentrations of PEO (typically in the literature, $>0.5\%$ PEO is used for birefringence studies). The shear rates were well above those reported in the literature, albeit these were in different geometries which bring other flow effects into play.

5. Conclusions and Summary

In summary the lack of observed birefringence in these setups could be due to:

- Insufficient path length through fluid (problem with detection)
- Instabilities in flow (no longer pure shear; problem with elongation)
- Insufficient time in flow for full extension of polymer chains (in oscillatory setup)
- Insufficient molecular weight of polymer samples (chain length)
- Chain scissions from excessive agitation- for example under high oscillatory shear- or expected time dependent decay (chain length)
- Insufficient shear rate to induce elongation (unlikely)

Many modifications of these setups were made during testing in order to address the above issues, some of which only further complicated the fluid behavior. For example, to improve path length in the oscillatory setup:

- Placed nearly parallel mirrors immediately above and below the shearing unit
- Constructed a reservoir attachment to enable larger gap widths
 - bubble formation unless top slide holder partially submerged
 - turbulent behavior when top slide holder partially submerged

No previous birefringence studies of aqueous PAAm solutions have, to the author's knowledge, been previously conducted. It is likely that in the setups tested here the path length was not long enough for the fluid layer to significantly affect the phase of the light passing through it. Considering then that this may already be a weak signal, recording the data via a CCD camera with a pixel depth higher than 8 bits would likely have increased the chances of detection. Furthermore, many of the general oscillatory flow birefringence studies in the literature detect the effect through the edge of the given fluid layer and submerge the oscillatory mechanism; thus, the path length (by design or accident) is typically longer, and enclosing the cell likely reduces some of the turbulent effects observed with both the reservoir and thin fluid layer versions of the oscillatory setup (no immediate liquid-air interface).

For a polymer with unknown birefringence, continuous shear is a better option for initial detection than oscillatory shear in that one does not need to worry that the oscillations might be interfering with the alignment of the polymer chains and can exclude the possibility that the shear might not have been applied over a sufficient amount of time for the polymer chains to fully extend.

6. Future Work

- Test with shear setups which allow longer path length (more significant phase change) and more stable, continuous flows (polymer chains more likely to align in the first place).

→ Fluid filled mill with two counter-rotating rollers (line of shear in between)

- Use polymers with higher molecular weights, as the effect typically becomes more pronounced with increasing chain length
- Use a more sensitive CCD camera or a photodiode
- Look into relation of birefringence onset to other solution properties (beginning of shear thinning behavior, etc), as these may be correlated. The onset of a previously studied effect may help to pinpoint the conditions under which the onset of another is most likely to occur.