

Background

PBDT and PBDI are water-soluble, charged polymers that differ by the exocyclic bond angle in their molecular structure, leading to dramatically different properties:

PBDT: Rigid Rods

Poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT) is a sulfonated polyamide. The poly condensation of TPC and BDSA results in a **linear polymer backbone that forms rigid rods**, through self-assemblies of helical dimers. The rods start to align at concentrations as low as 0.8wt%, causing nematic domains to form, visible under polarized light. PBDT shows **low viscosity at rest** but under **steady shear** (at a critical shear rate) it undergoes **irreversible gelation**.

PBDI: Kinked

PBDI (poly(2,2'-disulfonyl-4,4'-benzidine isophthalamide)) uses isophthaloyl chloride (IPC) as opposed to the TPC used in PBDT. The use of IPC (~120° exocyclic bond angle), **disrupting backbone linearity**. This is a **fully isotropic** system and does not form a liquid crystal. PBDI at ~7 wt% is a gel under no shear. PBDI exhibits **reversible shear-thinning under flow**.

Motivation

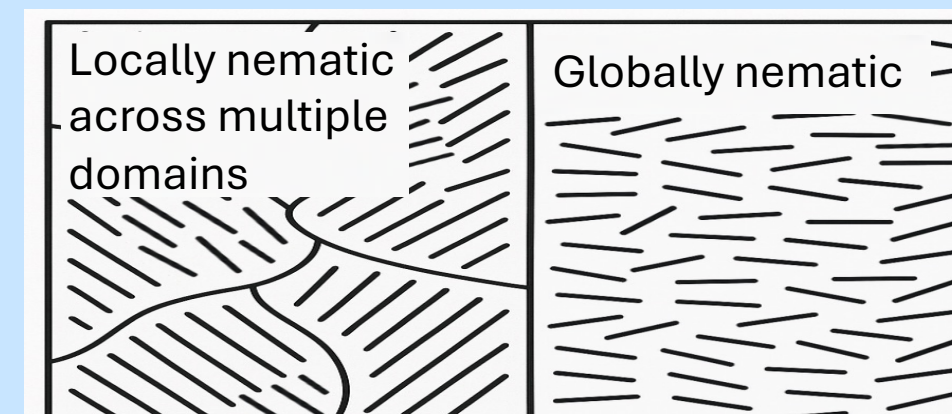
PBDT has been shown to **irreversibly gel** above a critical shear rate.

However, the rheological properties of **PBDI** have **never been studied**.

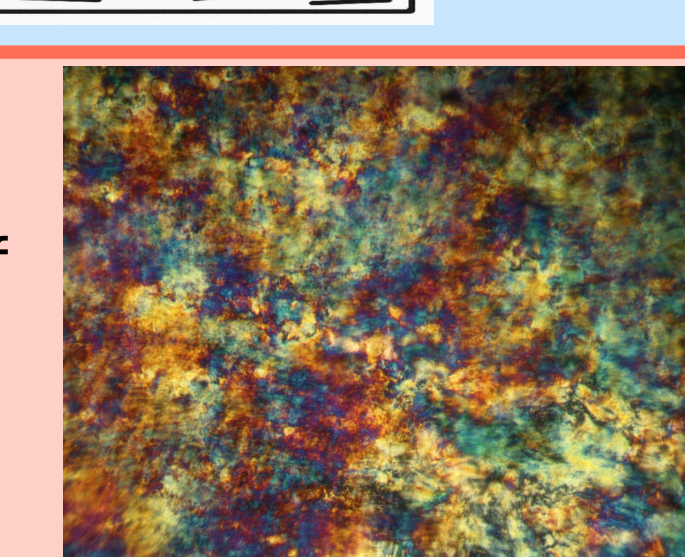
By comparing PBDT and PBDI aqueous solutions we can study the how **molecular geometry affects rheological properties** (under shear).

Liquid Crystals

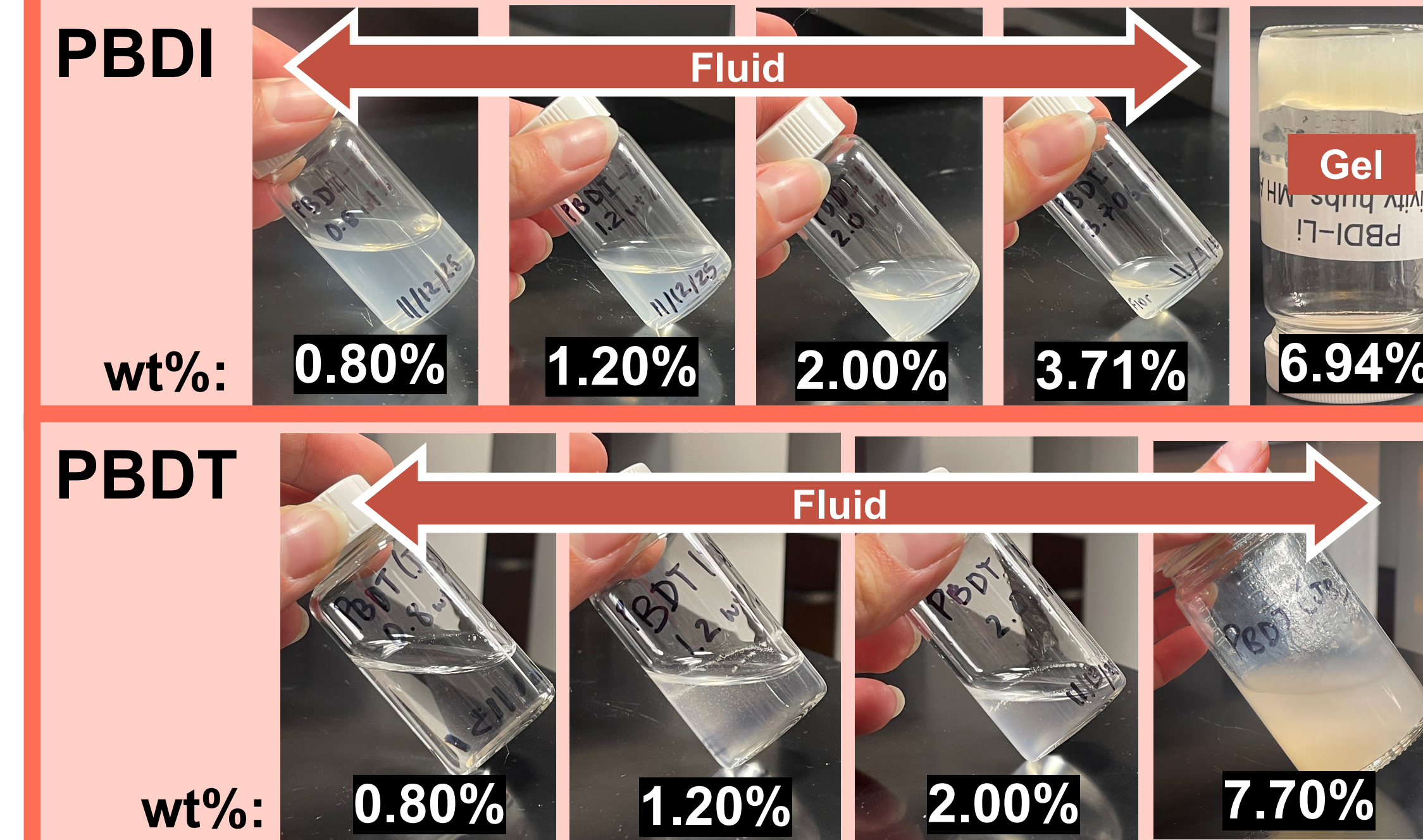
Liquid crystals are materials that flow like liquids but have **molecules aligned in ordered directions** like crystals.



PBDT is an example of a **Liquid Crystal**:



Sample Pictures



Synthesis (Ex. PBDI)

Step 1 (IPC Purification)



Crude isophthaloyl chloride (IPC) was purified by **sublimation**. IPC was heated to **95 °C** under **~13 mbar** vacuum, allowing it to **condense** as a solid on the cold finger. The purified IPC was collected and stored under dry conditions until use.

Step 2 (BDSA Purification)



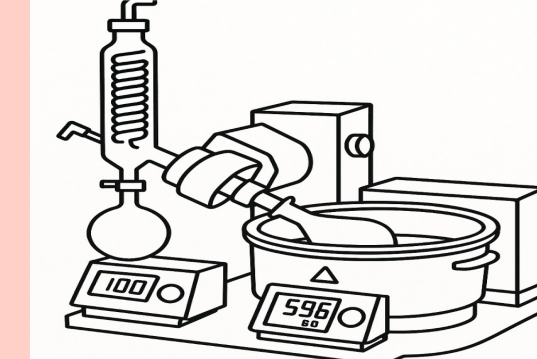
The diamine monomer, 4,4'-diaminobiphenyl-2,2'-disulfonic acid hydrate (95%) (**BDSA**) was purified via **repeated acid-base cycling**. The solid, crude, BDSA was dissolved in water and **neutralizing with Li₂CO₃**, liberating CO₂, and thus converting the BDSA into its **lithium salt form**, clearing the solution. The solution was then filtered, placed in an ice bath and **acidified with HCl**, reconvert the BDSA to its **acid form** (opaque white-pink in color). The solids precipitated and were isolated by vacuum filtration, after which the process starts all over again. This **neutralization → filtration → acidification** cycle was repeated four times to **remove impurities**, as indicated by the color change from pink to pale white-pink and the appearance of **shiny crystalline material**. The final acidic BDSA was collected as a powder and dried in a vacuum oven at 100–110 °C (vented with perforated aluminum foil) to remove residual water.

Step 3 (Blending)



The purified acidic **BDSA**, is added to a **high-shear Waring blender** along with water and neutralizing lithium carbonate. In a separate, argon-purged beaker, the **IPC** was dissolved in **chloroform** via stirring. This IPC/chloroform solution was added to the blender, along side the BDSA/Li₂CO₃, and blended for **~5 min**.

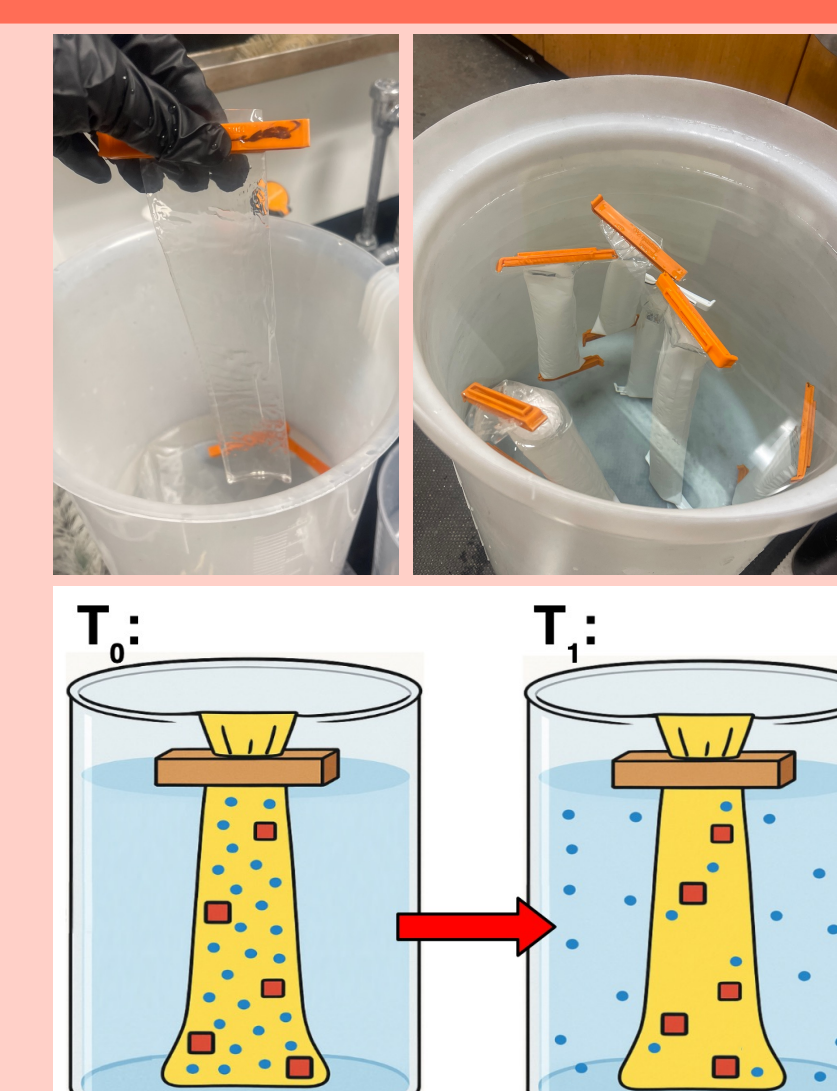
Step 4 (Removing Chloroform)



Chloroform was removed from solution via **rotary evaporation**.

Step 5 (Dialysis)

The solution was placed in **cellulose dialysis tubing** and **dialyzed against DI water** (which was periodically changed) to remove low-molecular-weight species and salts.



Step 6 (Drying)

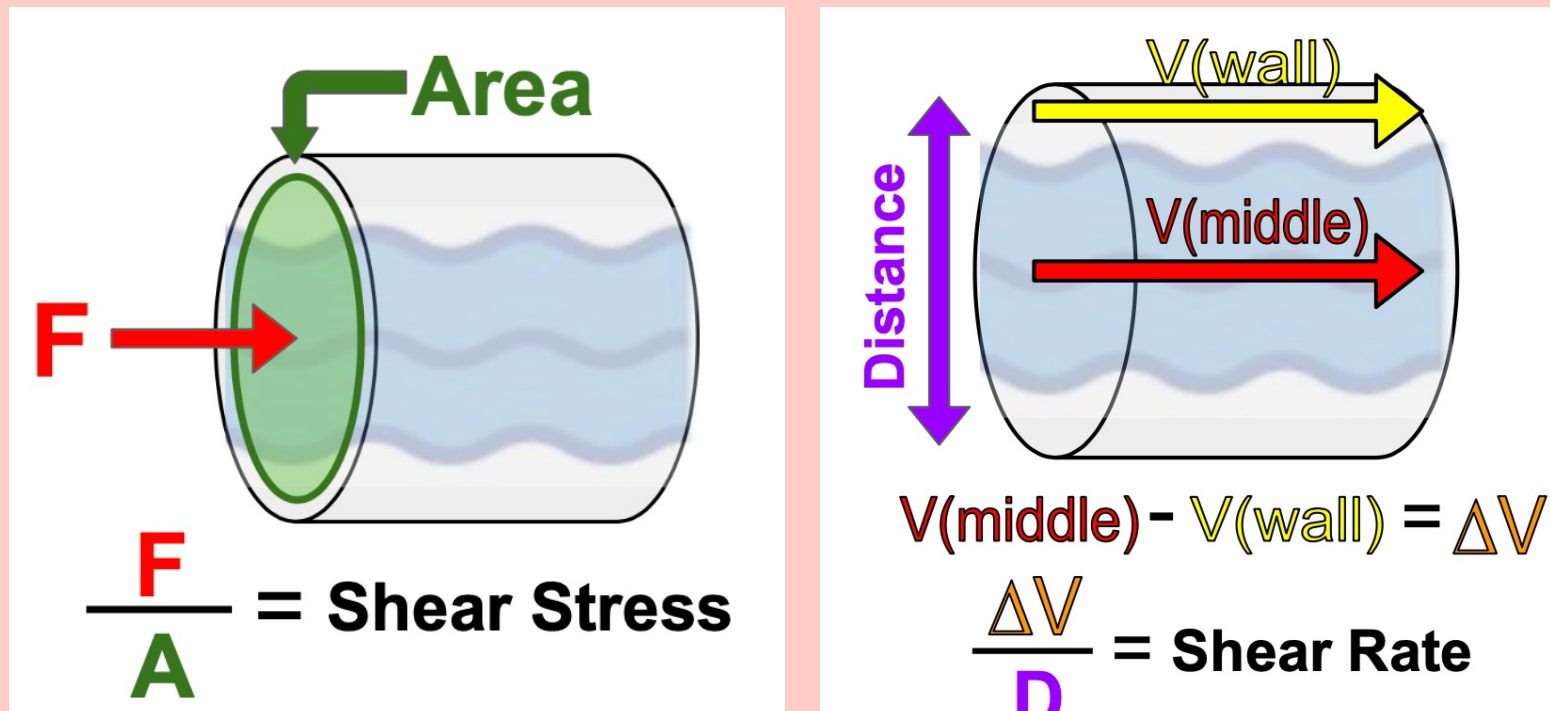
Sample was then dried in a **vacuum oven**. Removing excess water.



What Final Samples look like:



Rheology Basics



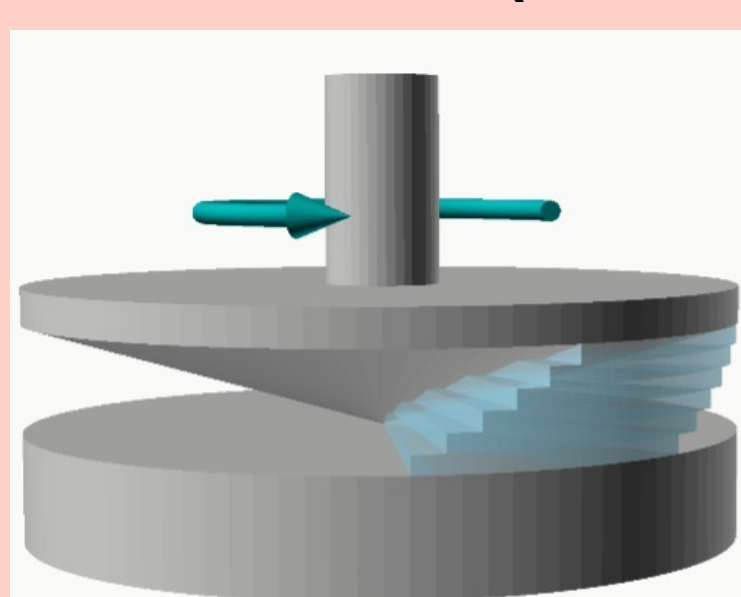
Rheology studies how materials **flow and deform** when **forces** are applied to them.

Shear Stress: the force per unit area applied to the material

Shear Rate: change in velocity divided by the distance; how fast the material deforms

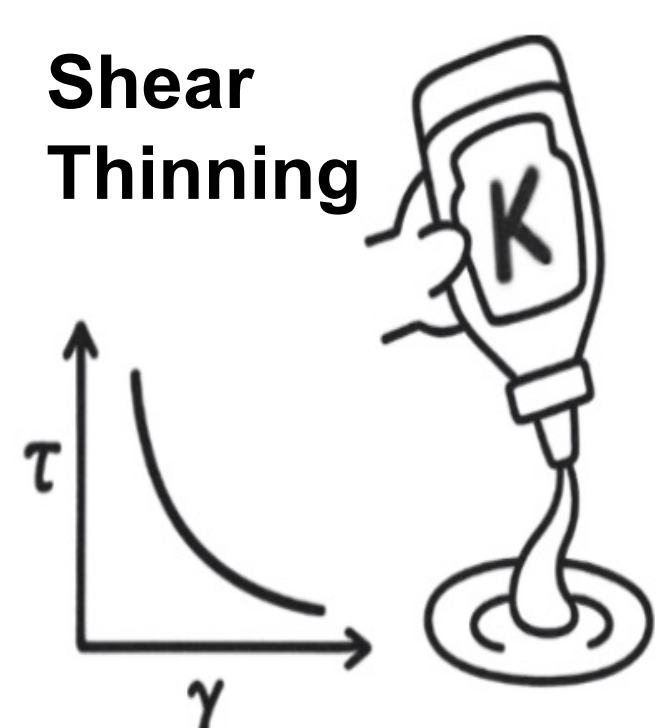
$$\frac{\text{Shear Stress } (\tau)}{\text{Shear Rate } (\dot{\gamma})} = \text{Viscosity } (\eta)$$

Rheometer (Cone and Plate)

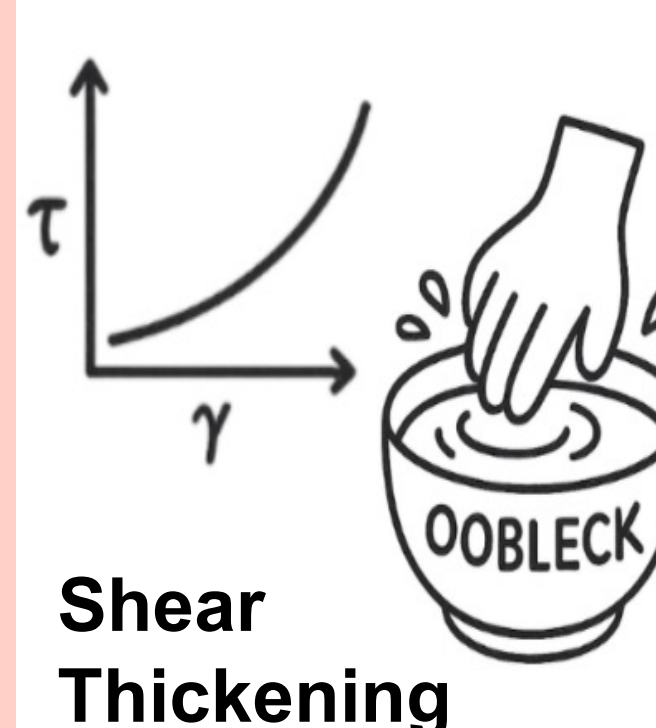


A rheometer is an instrument that **precisely controls either the stress or strain rate** applied to a sample. It measures **torque and deflection angle** in order to determine material characteristic such as **viscosity, elasticity and stress**.

Note: For most of our experiments we use either the **cone and plate** geometry or the concentric cylinders geometry.

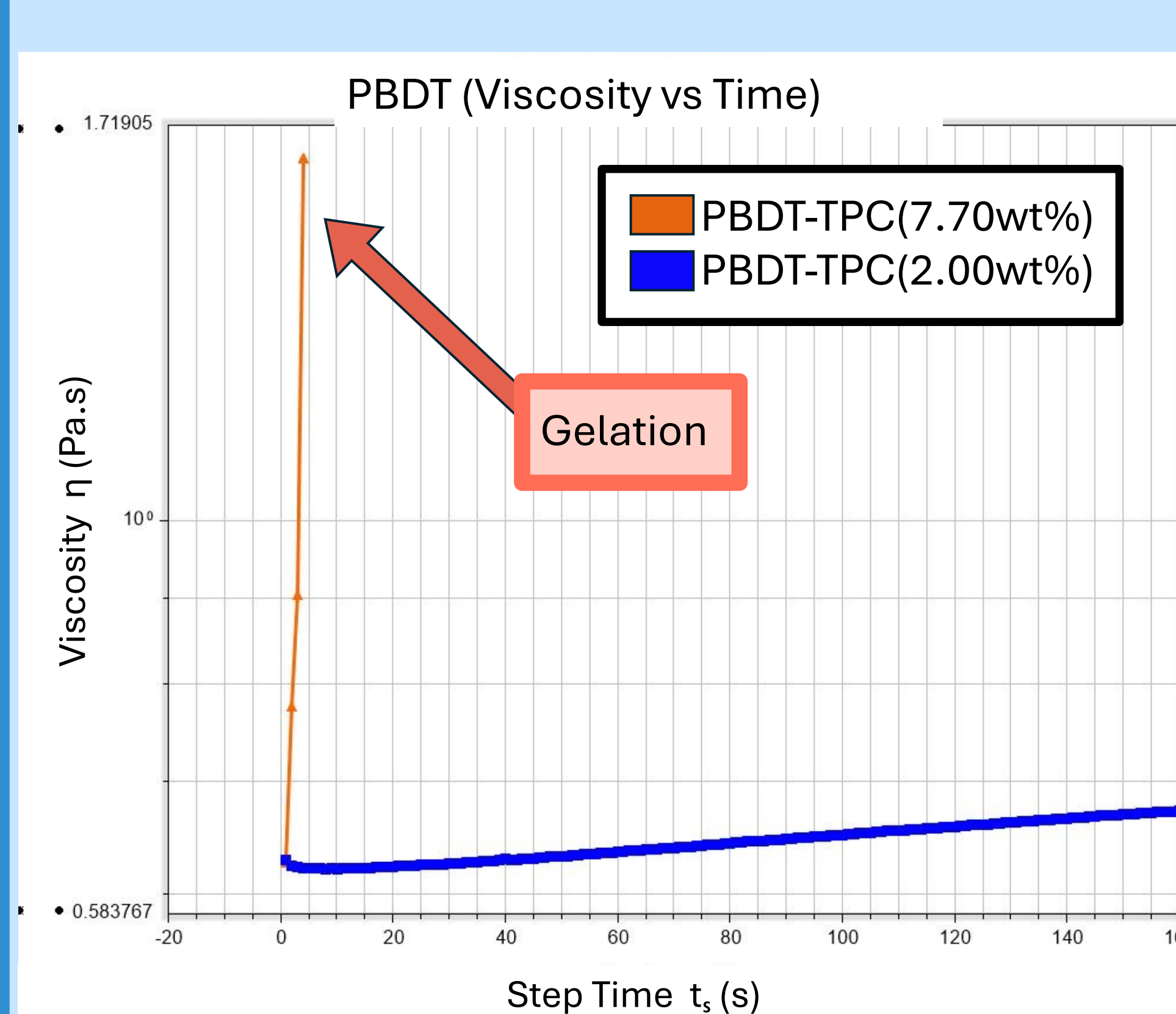


Shear-Thinning: **Viscosity decreases** with **shear rate**, meaning the fluid flows more easily the faster you shear it. Ex. Ketchup

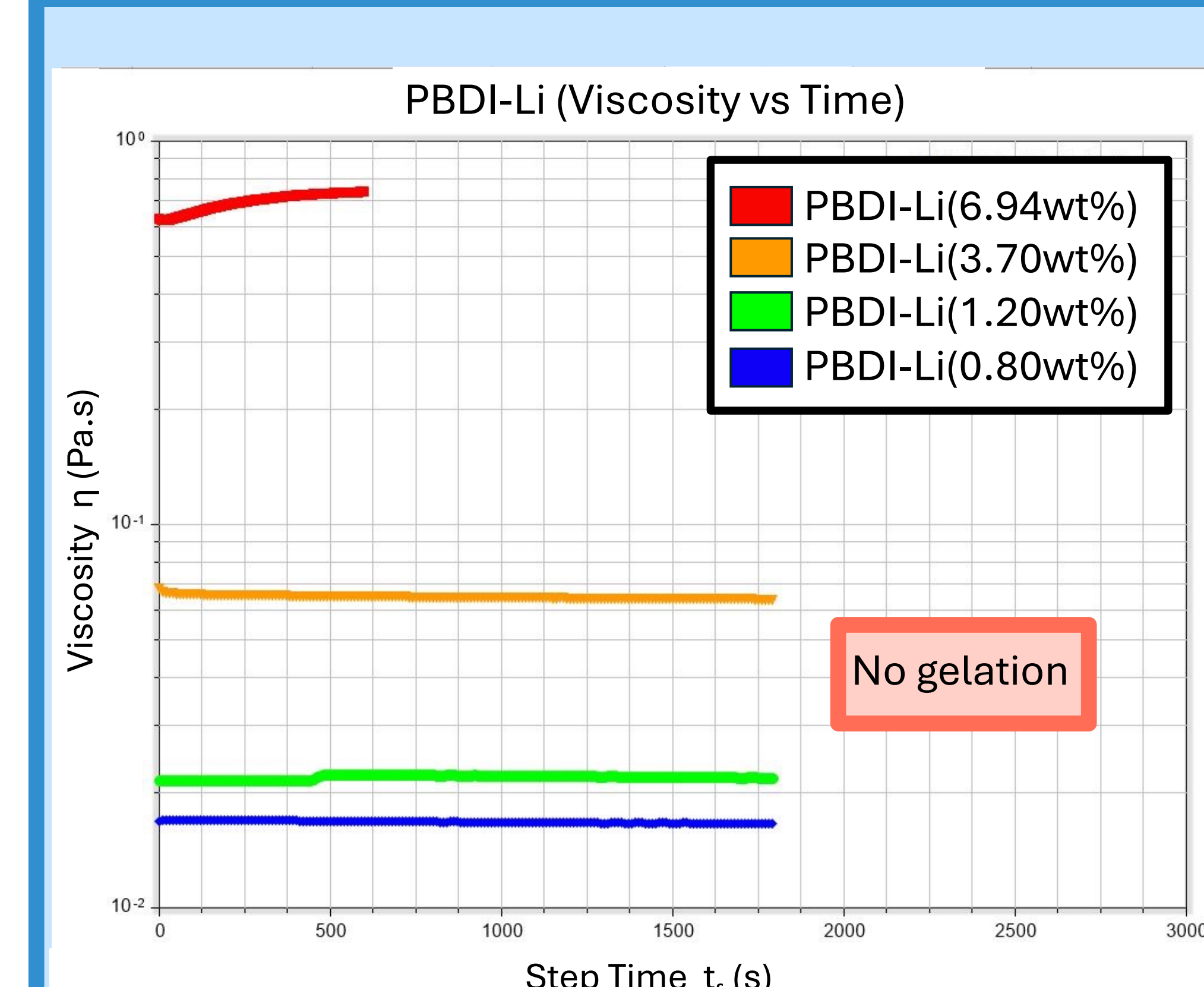


Shear-Thickening: **Viscosity increases** with **shear rate**, meaning the fluid becomes harder to deform the faster you shear it. Ex. Oobleck

Rheology of PBDT



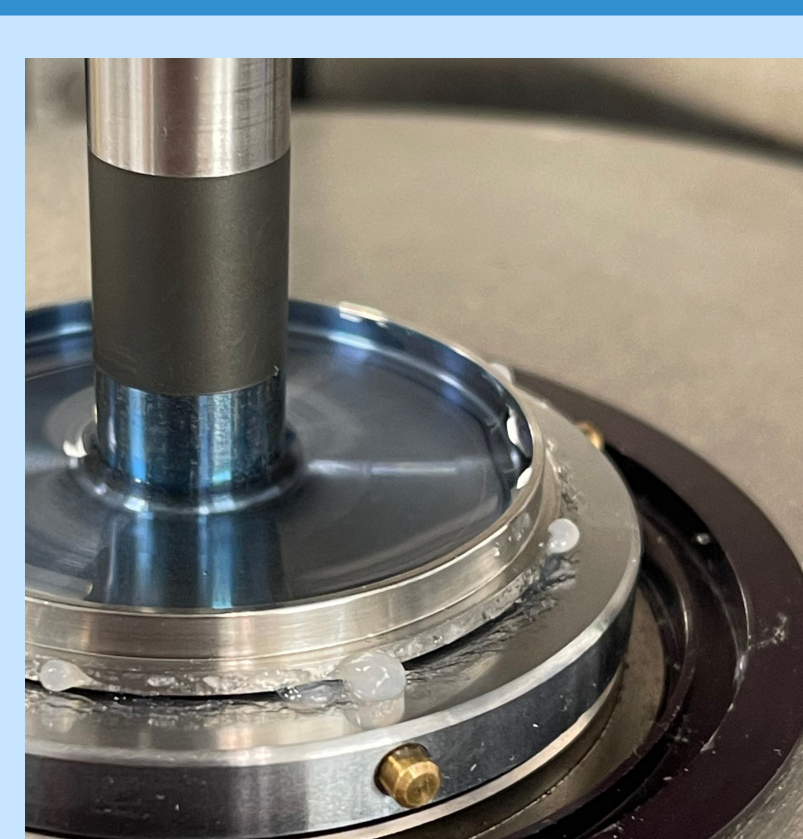
Rheology of PBDI



Gelation Pictures



This picture is of a sample of **PBDT** gelled at a shear rate of 1500 1/s. This is an irreversible gel. Reproduced from Fox, R.J. et al. ACS Macro Lett. 2020, 9, 957-963.



This is a picture taken of **PBDT** after it irreversibly gelled, within seconds, at a shear rate of 1000 1/s.

Polarized Optical Microscope Images

PBDI

wt%: 0.80%

1.20%

2.00%

6.94%

PBDT

wt%: 0.80%

1.20%

2.00%

7.70%

References

Irreversible Shear-Activated Gelation of a Liquid Crystalline Polyelectrolyte
Ryan J. Fox, Maruti Hegde, Curt J. Zanelotti, Amar S. Kumbhar, Edward T. Samulski, Louis A. Madsen, Stephen J. Picken, and Theo J. Dingemans
ACS Macro Letters 2020 9 (7), 957-963
DOI: 10.1021/acsmacrolett.0c00168

Solution properties of a rod-like polyelectrolyte: Role of rod-length and polymer chain end-groups
Migliore, John and Hegde, Maruti and Dingemans, Theo
Polymer 2025 338, 128988
DOI: <https://doi.org/10.1016/j.polymer.2025.128988>

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