School of Engineering
Institute of Materials
Laboratory of Macromolecular
and Organic Materials (LMOM)

Polymer Science (MSE-360)

Melt Rheology

Semester 2025/26

Assistant:

Sarah Marroquin Burgos (LMOM, MXG 038)

sarah.marroquinburgos@epfl.ch

Introduction

Polymers exhibit pronounced viscoelastic behavior near their thermal transitions, such as the glass transition temperature (T_g) or the onset of the rubbery plateau. In these regimes, the mechanical response depends not only on temperature but also on time and deformation rate (or oscillation frequency). For thermorheologically simple polymers, i.e. materials whose relaxation mechanisms share the same temperature dependence and do not undergo structural changes in the observed temperature range, the viscoelastic response at different temperatures can be related through *time–temperature superposition* (TTS): raising the temperature has an effect equivalent to probing longer timescales (lower frequencies) at constant temperature.

In this TP, the melt properties of polystyrene (PS) will be characterized by small-amplitude oscillatory shear rheology. First, the linear viscoelastic regime (LVR) will be determined by amplitude sweeps, followed by temperature sweeps at constant frequency and frequency sweeps at several temperatures to enable construction of a master curve via TTS. From the master curve, shift factors will be extracted and analyzed, and the entanglement density of PS will be estimated from the plateau modulus.

Measurement Principles and Fundamental Relations

A rotational rheometer applies a controlled deformation (or stress) to a sample placed between two surfaces (e.g. two parallel plates, or cone–plate) and measures the resistance to flow (Figure 1).

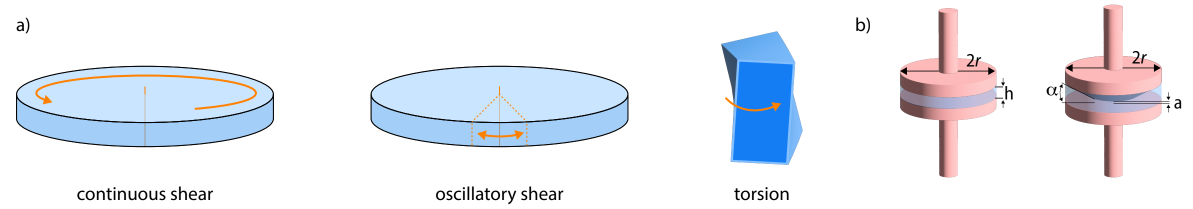

Fig. 1. a) Modes of deformation in standard rheology experiments. b) Common measuring systems for shear rheology: parallel plate (left) with diameter 2r and gap height h; cone-plate (right) with diameter 2r, cone angle α, and truncation gap a.

The instrument records three primary signals:

- The **torque**, $\boldsymbol{M}$ (unit: $\mathrm{N \cdot m}$), quantifies how a force f applied at a distance r from the rotation axis produces rotation:

$$M = \mathrm{r \cdot f \cdot} \sin\theta \quad (\text{for } 90°, M = \mathrm{r \cdot f}) \ . \tag{1}$$

- The **angular displacement**, $\boldsymbol{\theta}$, is the rotation angle given in radians (rad, with $1° = \mathrm{rad}\ \frac{180}{\pi}$), related to arc length, s, and radius, r:

$$\theta = \frac{s}{r} \ . \tag{2}$$

- The **angular velocity**, $\boldsymbol{\Omega}$ (unit: rad/s), is the change in angular displacement per unit time:

$$\Omega = \frac{\Delta\theta}{\Delta t} \ . \tag{3}$$

From these signals, the instrument calculates the rheological parameters shear stress $\boldsymbol{\sigma}$, shear strain $\boldsymbol{\gamma}$, and shear rate $\dot{\boldsymbol{\gamma}}$.

- The **shear stress, $\boldsymbol{\sigma}$** (unit: Pa or Dyne/cm^2) is derived from the torque via a geometry-dependent stress constant, K_σ, which takes measurement geometry and sample dimensions into account:

$$\sigma = M\, K_\sigma \ . \tag{4}$$

- The **shear strain, $\boldsymbol{\gamma}$** (dimensionless) measures the relative deformation, and is derived from the angular displacement and a geometry-specific strain constant, K_γ:

$$\gamma = \theta\, K_\gamma \ . \tag{5}$$

- The **shear rate, $\dot{\boldsymbol{\gamma}}$** (unit: s^{-1}) follows analogously from the angular velocity:

$$\dot{\gamma} = \Omega\, K_\gamma \ . \tag{6}$$

Thus, **the measurement geometry defines how torque, displacement, and velocity are converted into stress, strain, and shear rate, and thereby into material functions such as modulus and viscosity:**

$$G = \frac{\sigma}{\gamma} = \frac{MK_\sigma}{\theta K_\gamma} \ , \quad \eta = \frac{\sigma}{\dot{\gamma}} = \frac{MK_\sigma}{\Omega K_\gamma} \ . \tag{7, 8}$$

The most common geometries are **parallel plate** and **cone-plate** systems (Figure 1b) which differ in how shear varies with radial position. In cone-plate geometry, the narrowing gap produces a uniform shear rate across the sample. In contrast, for parallel plates, the local shear rate increases linearly from the center to the rim. Under the assumptions of no slip, complete sample filling, and linear response (see below), the conversion constants for parallel plates are $K_\sigma = 2/(\pi r^3)$ and $K_\gamma = r/h$. Accordingly, the effective stress increases with plate radius, and the shear rate increases as the gap h decreases. As a rule of thumb, large diameters (larger contact area) are best for low-viscosity fluids, while smaller diameters are preferable for high viscosity or solid-like samples.

Practical caveats and experimental assumptions:

- **Small-angle/small gap approximations:** the cone angle must be small and the parallel-plate gap h must be small relative to radius for the simple formulae to hold. Truncated cones require a truncation correction.
- **Edge vs. average values:** parallel-plate strain and shear rate vary with *r*; the quantities above are rim (edge) values unless stated otherwise.
- **Truncation gap and particles:** cone-plate truncation gaps are typically a = 20–120 µm. Samples with particles must have particle size $\ll a$ (rule of thumb: gap > 10 x particle size) to avoid crushing or artifacts.

- **Contact and trimming:** ensure full contact (no gaps or air bubbles) and consistent trimming. Small changes in sample geometry change the conversion constants.
- **Slip and wall effects:** polymer melts can slip at smooth boundaries. Use sandblasted or roughened geometries where appropriate and check for slip.
- **Instrument sensitivity and inertia:** at very low torques the instrument noise and compliance matter. At high frequencies inertial effects of the geometry become significant. Consult instrument torque and inertia limits when planning frequency sweeps.
- **Temperature control and thermal expansion:** thermal expansion of the tool and sample can change the gap. Set and monitor axial force/normal force where available.

Rheological Experiments

Rheometers allow several types of experiments to probe the flow and deformation behavior of materials:

- **steady shear (flow tests):** a constant shear rate is applied and the viscosity η is measured.
- **transient tests:** include **stress relaxation** experiments, where a sudden strain is applied and the subsequent stress decay is recorded, and **creep and recovery**, where a constant stress is applied, and the evolution of strain is monitored; upon stress removal, recovery can be followed.
- **oscillatory shear (dynamic tests):** a sample is subjected to periodic stress or deformation, generally of sinusoidal form, which allows one to separate the viscoelastic response into elastic and viscous contributions.

The focus of this TP lies on oscillatory shear experiments which are described in more detail in the following. Whether stress or strain is controlled depends on the instrument. In strain-controlled oscillatory shear, the applied deformation is given by:

$$\gamma = \gamma_0 \sin(\omega t) \ , \tag{9}$$

with strain amplitude γ_0 and angular frequency ω. The stress response is phase-shifted by an angle δ, and can be decomposed into an **in-phase (elastic)** and an **out-of-phase (viscous)** component:

$$\sigma = \sigma_0 \sin(\omega t + \delta) = \sigma_0(\sin \omega t \cos \delta + \cos \omega t \sin \delta). \tag{10}$$

Dividing by γ_0 gives the time-dependent shear modulus:

$$G(t) = \frac{\sigma}{\gamma_0} = \frac{\sigma_0}{\gamma_0}(\sin \omega t \cos \delta + \cos \omega t \sin \delta) = G' \sin \omega t + G'' \cos \omega t \ . \tag{11}$$

Here, *G'* and *G''* are the "storage modulus" and the "loss modulus", respectively. *G'* reflects the elastic response (energy stored and recovered), while *G''* characterizes the viscous response (energy dissipated by internal friction during flow). Their ratio defines the loss factor:

$$\tan \delta = \frac{G''}{G'} \ , \tag{12}$$

which quantifies the balance between elastic and viscous behavior: a large $\tan\delta$ indicates a more dissipative, viscous material. For ideally viscous behavior ($\delta = 90°$), G' = 0 (there is no elastic portion). For ideally elastic behavior ($\delta = 0°$), G'' = 0 and the loss factor vanishes.

Depending on the measurement type, the stress is typically measured as a function of strain (at constant temperature and frequency), at constant temperature T (constant frequency and strain) or as function of ω (constant temperature and strain).

Amplitude Sweeps

Amplitude sweeps are used to determine the **linear viscoelastic regime (LVR)**, where the material structure is not destroyed by the applied deformation. In this regime, viscoelastic functions are independent of stress or strain amplitude. During an amplitude sweep, the strain amplitude γ_0 is stepwise increased while the frequency ω is kept constant (Figure 2a). In the LVR, both G' and G'' remain constant. Beyond the LVR limit, moduli deviate from their plateau values, indicating structural changes of the sample (Figure 2b).

Because the LVR shrinks with decreasing temperature and increasing frequency, an amplitude sweep must always be performed before other oscillatory tests. For subsequent experiments, the applied strain should be chosen within the LVR. Measurements at larger deformations are beyond the scope of this TP, although they are important for practical applications (e.g. polymer processing).

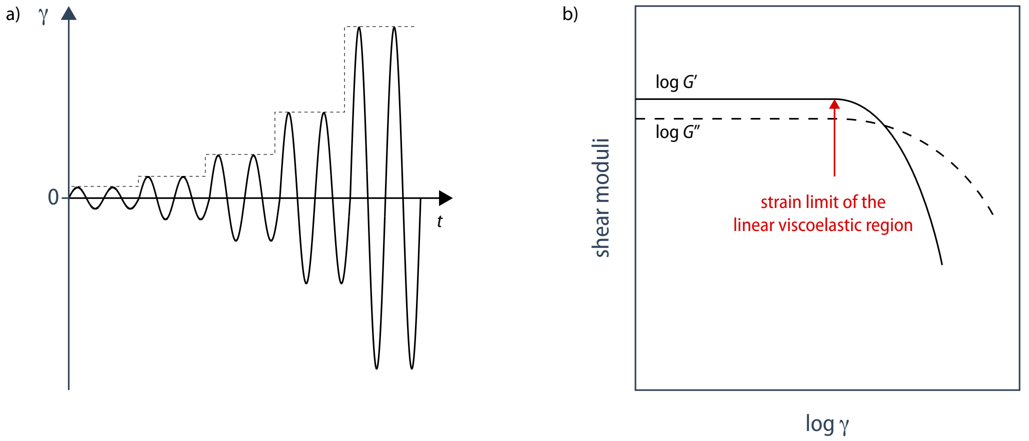

Fig. 2. a) Preset of an amplitude sweep at controlled strain with an increase in the amplitude in five steps. Frequency is kept constant at all five measuring points. b) Result of an amplitude sweep, the functions of G’ and G’’ show constant plateau values within the linear viscoelastic region.

Temperature-dependent Measurements

Temperature sweeps are performed at constant amplitude and frequency. They reveal how viscoelastic properties evolve with temperature and allow correlations with molecular structure (e.g. molar mass, dispersity, or crosslinking) (Figure 3). Temperature sweeps also identify transition regions (e.g. glass transition, softening) and provide modulus-dependent relationships. Such information is useful for optimizing experimental parameters (axial force, strain, etc.) prior to long-term time-temperature superposition (TTS) experiments.

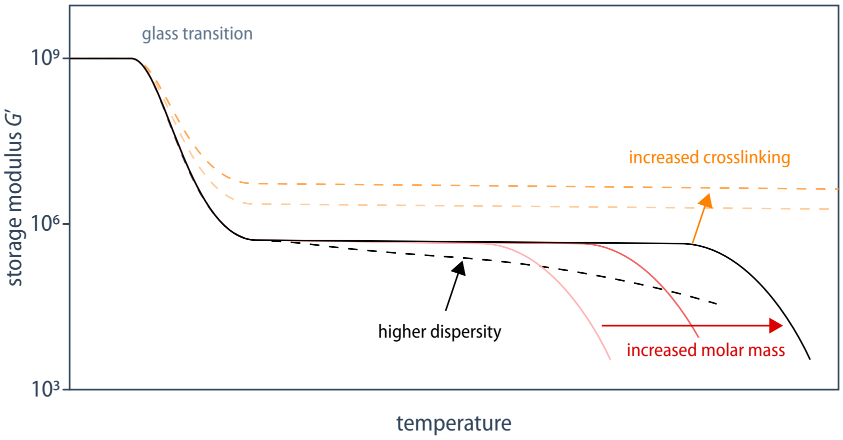

Fig. 3. Idealized temperature sweep of an amorphous polymer with indicated influence of molar mass, dispersity, and crosslinking.

Frequency Sweeps and Time-Temperature Superposition

Frequency sweeps probe the materials response as a function of oscillation frequency at constant strain amplitude and temperature. However, the frequency window of a rheometer is limited: low-frequency measurements require very long times, while high-frequency data may be distorted by instrument inertia. To extend the accessible range, the **time-temperature superposition (TTS) principle** can be applied, which relies on the fact that linear viscoelastic properties depend on both time and temperature:

- increasing the temperature accelerates relaxation processes, equivalent to probing shorter timescales (higher frequencies).
- Decreasing the temperature slows relaxation, equivalent to probing longer timescales (lower frequencies)

For **thermorheologically simple polymers** (e.g. polystyrene melts), where all relaxation modes share the same temperature dependence and no structural changes occur in the observed temperature range, frequency sweeps at different temperatures can be shifted horizontally along the frequency axis (log scale) to construct a **master curve** (Figure 4). This curve spans many decades in time and frequency, allowing prediction of behavior in otherwise inaccessible regimes:

- low-frequency regime (from high-T data): provides information relevant to creep, stress relaxation, long-term aging.
- high-frequency regime (from low-T data): corresponds to short-time responses such as high-speed impacts, mechanical vibrations, or acoustic excitations.

The horizontal shift factors a_T describe the frequency displacement required to superimpose the curves. Near the glass transition, they typically follow the empirical **Williams-Landel-Ferry (WLF) equation**:

$$\log a_T = -\frac{C_1(T-T_{\mathrm{ref}})}{C_2+T-T_{\mathrm{ref}}}, \qquad (12)$$

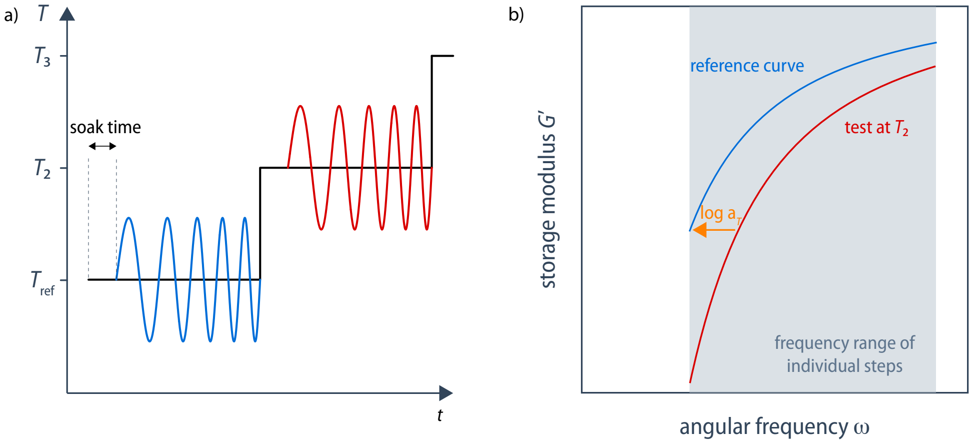

Fig. 4. Experimental principles of TTS. a) oscillatory measurement/frequency sweeps are applied at different constant temperatures. The material response is monitored over a practically feasible frequency range, at a constant amplitude of deformation. b) Individual curves are horizontally shifted in log space with respect to a reference temperature.

with empirical constants C_1 and C_2. Typical values for C_1 and C_2 are in the range 8–14 and 30–50 K, respectively, but if T_g is chosen as the reference temperature, nearly universal values ($C_1 = 17.44$ and $C_2 = 51.6$ K) are found for many amorphous polymers. The WLF equation is most accurate close to T_g, where relaxation dynamics are governed by free volume effects.

At temperatures well above T_g, the WLF equation reduces to an **Arrhenius-type behavior**, suitable for thermally activated processes. The viscosity is then expressed as:

$$\eta(T) = A \cdot e^{(E_a/\mathrm{R}T)} \ , \tag{13}$$

where E_a is the activation energy for flow, R is the gas constant, and A a pre-exponential factor. Because the shift factor a_T can be defined as the ratio of relaxation times (or equivalently viscosities) at T and at a reference temperature T_{ref},

$$\mathrm{a}_T = \frac{\eta(T)}{\eta(T_{\mathrm{ref}})} \ , \tag{14}$$

one obtains the **Arrhenius form for the shift factor**:

$$\ln \mathrm{a}_T = \frac{E_a}{\mathrm{R}} \left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}} \right) \ , \tag{15}$$

Thus, plotting $\ln \mathrm{a}_T$ versus reciprocal temperature (in Kelvin) yields a straight line with slope E_a/R and intercept $-E_a/(\mathrm{R}T_{\mathrm{ref}})$(Arrhenius plot), from which the activation energy of the relaxation process can be extracted. The Arrhenius representation is particularly useful above the glass transition, where relaxation follows simple activated dynamics, but may also be applied near T_g to characterize the activation energy associated with segmental relaxation.

Limitations of TTS

TTS requires thermorheologically simple behavior. Limitations include:

- valid only if all relaxation processes have the same temperature dependence.

- therefore, this approach is often limited to temperature ranges close to the glass transition.
- not valid in the glassy state.
- not applicable to nonlinear viscoelastic behavior (large strains).
- invalid for multiphase systems (blends, composites), filled polymers, or materials undergoing structural changes (e.g. crystallization, curing, degradation).

The validity can be checked by:

- Van Gurp–Palmen and Cole–Cole plots (should give smooth curves).
- shift factors should fit the WLF or Arrhenius equation.
- consistent shift factors across all viscoelastic parameters (G', G'', tan δ).

If any of these criteria are not met for a given material, TTS may not be applicable.

Experimental Part and Discussion

The goal of this TP is to characterize the melt properties of polystyrene (PS) by rheological measurements, including the construction of a time-temperature superposition (TTS) master curve.

Polystyrene is chosen as a model system because it is a thermorheologically simple: it is amorphous (does not crystallize), has well-defined segmental relaxation dynamics, and is technologically relevant as a base polymer in many applications.

Tasks:

1. **Determine the linear viscoelastic regime (LVR):**
    - Perform amplitude sweeps at different temperatures and frequencies.
    - Identify the strain amplitude up to which G' and G'' remain constant.
    - Select an appropriate strain amplitude within the LVR for your subsequent oscillatory tests. Explain your choice.
2. **Record temperature-sweeps at two different frequencies:** 1 rad/s and 100 rad/s.
    - Observe how G', G'', and tan δ evolve with temperature.
    - Compare the two curves and relate the differences to relaxation dynamics.
3. **Frequency sweeps for Master Curve Construction**
    - Perform frequency sweeps at different temperature between 115 and 240 °C, spaced at 15 °C.
    - Use a strain amplitudes within the LVR.
    - What general trends do you observe in G' and G'' as frequency increases?
4. **Master Curve Construction (TTS)**
    - Plot the frequency sweeps at different temperatures.
    - Horizontally shift the curves “by eye” (along the log frequency axis) to superimpose them onto the reference curve (choose a T_{ref} close to T_g + 50 °C).
    - Comment on the global viscoelastic behavior seen in the master curve.

- Create a van Gurp–Palmen plot (phase angle vs. complex modulus) and discuss the result.
- Extract the horizontal shift factors a_T, plot and fit them according to the WLF ($\log a_T$ vs. T) and Arrhenius equation ($\ln a_T$ vs. $1/T$).
- Are there deviations from linearity (in the Arrhenius plot) or from the universal WLF constants? What does this reveal about the relaxation processes of polystyrene?

5. Rubbery State and Entanglement Density

- Identify the rubbery plateau modulus, G_N^0, from your master curve (typically at the minimum of $\tan\delta$).
- Use the following relation to estimate the molar mass between entanglements (M_e) in the rubbery state:

$$G_{N0} = \rho \mathrm{R} T / M_e \ , \qquad (16)$$

- Compare your values to literature data for polystyrene.

Report Guidelines:

- How did you determine the strain amplitude for frequency sweeps at different temperatures?
- What differences did you observe between the two temperature sweeps (1 rad/s vs. 100 rad/s)?
- Discuss the global behavior from your master curve and identify different regimes.
- How valid was the TTS approach for your data (based on van Gurp–Palmen and shift-factor fits)?
- Compare WLF and Arrhenius fits of your shift factors. What physical mechanisms do they reflect?
- Explain the origin of the rubbery state in PS and provide your calculated entanglement density.

Additional Reading

V. Dorléans, R. Delille, D. Notta-Cuvier, F. Lauro, E. Michau. Time-temperature superposition in viscoelasticity and viscoplasticity for thermoplastics. *Polymer Testing* **2021**, *101*, 107287.

H. Ramli, N. F. A. Zainal, M. Hess, C. H. Chan. Basic principle and good practices of rheology for polymers for teachers and beginners. Chem. Teach. Int. **2022**, *4*, 307-326.

S. Liu, Y. Wang, V. Hirschberg, H. Shen, T. Cui, Q. Huang. Comparison of Shear and Extensional Rheology between Entangled Star and Linear Polystyrenes with the Same Span Molecular Weight. *Polymer* **2025**, 129148

M. Rubinstein, R.H. Colby, Polymer physics, Oxford university press, **2003**.