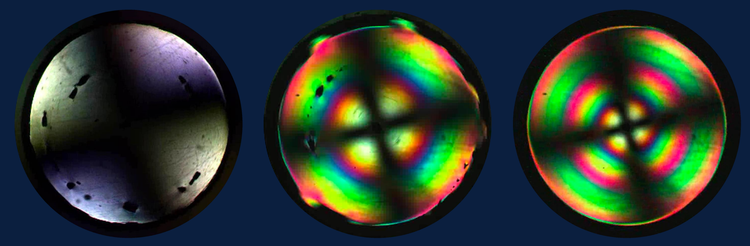
Shear-Induced Nematic Alignment in Polysulfone Melts

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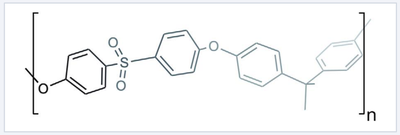


Polarized-light images of the sheared melt at 285 ° C: colour fringes are aligned chains

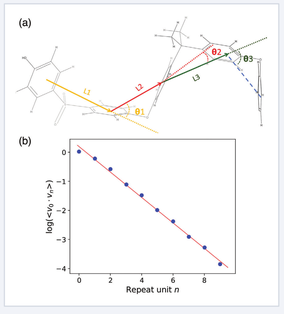
1 Why it matters

- Melt processing puts polymers through intense shear and cooling. The flow-induced structure sets the properties of the final part.
- Knowing **where alignment switches on**, in temperature and shear rate, is what processing windows are built from.

2 A semiflexible chain, isotropic at rest



PSU S3010 (BASF)
M_w = 59 kg/mol, M_w/M_n = 1.4
T_g = 191 ° C, stable to 403 ° C
No transition from T_g to 360 ° C



KUHN LENGTH

6.6 nm

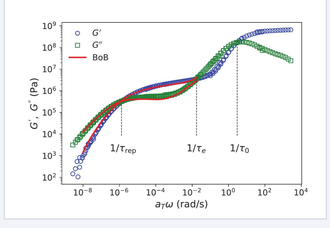
semiflexible: between flexible polyolefins (≈1 nm) and rod-like PEEK (≈10 nm)

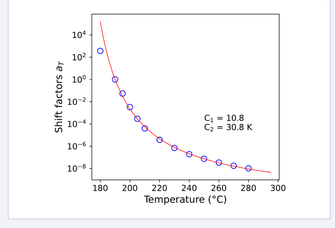
OVERLAP VOLUME FRACTION

9.6

above Onsager's critical value of 5.3, so shear can bring the chains into nematic order

3 Relaxation times from linear rheology





T (° C)	τ_e (s)	τ_R (s), Rouse	τ_{rep} (s), reptation
250	4.18×10^{-6}	1.92×10^{-2}	1.00
285	4.00×10^{-7}	1.84×10^{-3}	9.63×10^{-2}
320	1.06×10^{-7}	4.89×10^{-4}	2.56×10^{-2}

Longest chains, $M_{99\%}$ = 160 kg/mol. The tube-model (BoB) fit at 190 ° C gives τ_e = 57.3 s and M_e = 2.36 kg/mol; $\tau_R = \tau_e(M/M_e)^2$. WLF shift factors (C_1 = 10.8, C_2 = 30.8 K) carry the times to each temperature.

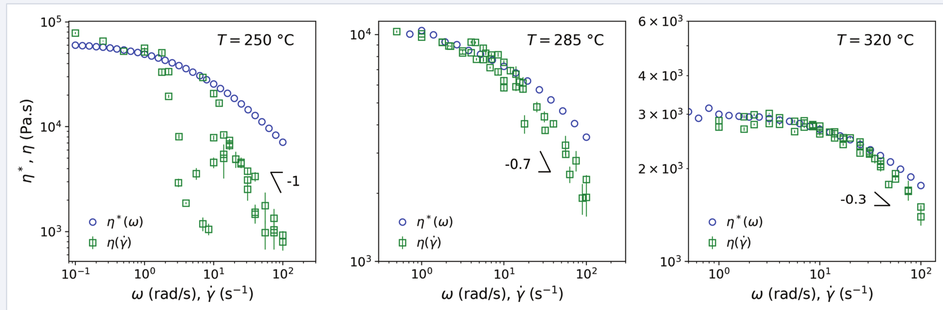
≈50×

lower onset shear rate (I/II border)

Polysulfone melts align under shear far sooner than chain stretching predicts.

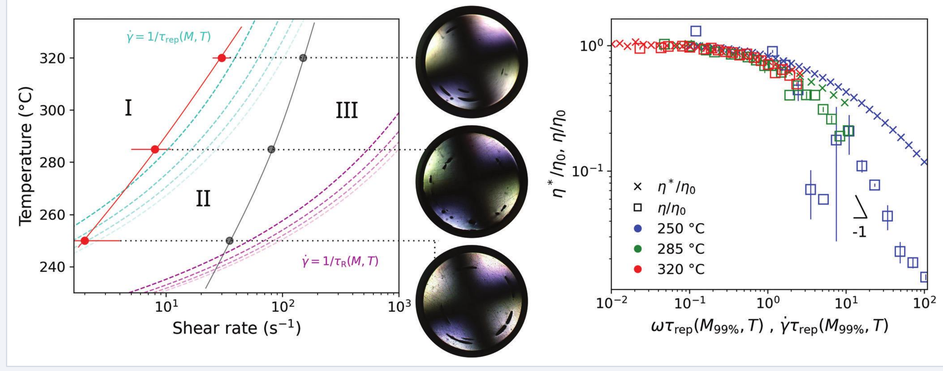
Our hypothesis: π–π stacking between phenyl groups adds an enthalpic contribution that stabilizes aligned chains.

4 The Cox–Merz rule fails above a critical shear rate



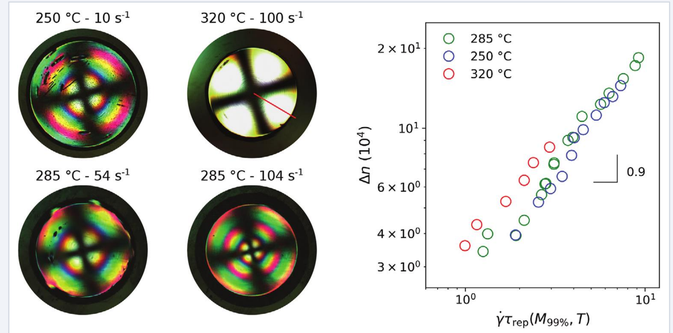
Steady-shear viscosity η (green), from steady states in start-up of shear, drops below the complex viscosity η^* (blue). At 250 ° C it falls as 1/shear rate, the signature of an isotropic–nematic biphase. The critical rate rises with temperature.

5 Temperature–shear rate map of alignment



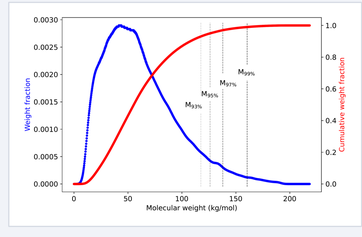
I I/II boundary (red): the Cox–Merz rule first fails and birefringence becomes easy to quantify. **II/III boundary** (grey): where full nematic alignment is expected, but edge fracture prevents us from observing it. Dashed: $1/\tau_{rep}$ (cyan) and $1/\tau_R$ (magenta) of the longest chains. **Middle:** rheo-optical (SIPLI) images at the I/II boundary. **Right:** all temperatures collapse when rescaled by τ_{rep}.

6 Birefringence confirms nematic alignment



Rheo-optical imaging (SIPLI) in parallel plates: colour fringes give Δn through the Michel–Lévy chart. Δn climbs steadily above Wi = 1 with an exponent of 0.9, against 0.5 for a fully nematic melt. The alignment is partial.

7 The longest chains set the onset



WI (REPTATION) AT ONSET

≈ 1

the same at every temperature

WI (ROUSE) AT ONSET

≈ 0.019

about 50× too early for stretching

GPC: 99% of the chains are shorter than $M_{99\%}$ = 160 kg/mol. The reptation time of these chains matches the onset at 250, 285 and 320 ° C; their Rouse time predicts shear rates about 50× too high.

8 Conclusions and next steps

- Shear aligns PSU chains: Cox–Merz failure and strong birefringence set in together.
- Alignment starts ≈50× sooner than stretching allows. **Hypothesis:** an enthalpic contribution from π–π stacking of phenyl groups.
- Next: X-ray scattering and other molecular weights to test this hypothesis against an orientation-only mechanism.

Reference. S. Daryoush, T. Outerelo Corvo, E. D. Gomez, R. H. Colby, *Adv. Funct. Mater.* 2025, 35, 2419750. doi.org/10.1002/adfm.202419750. Contact: rhc5@psu.edu

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