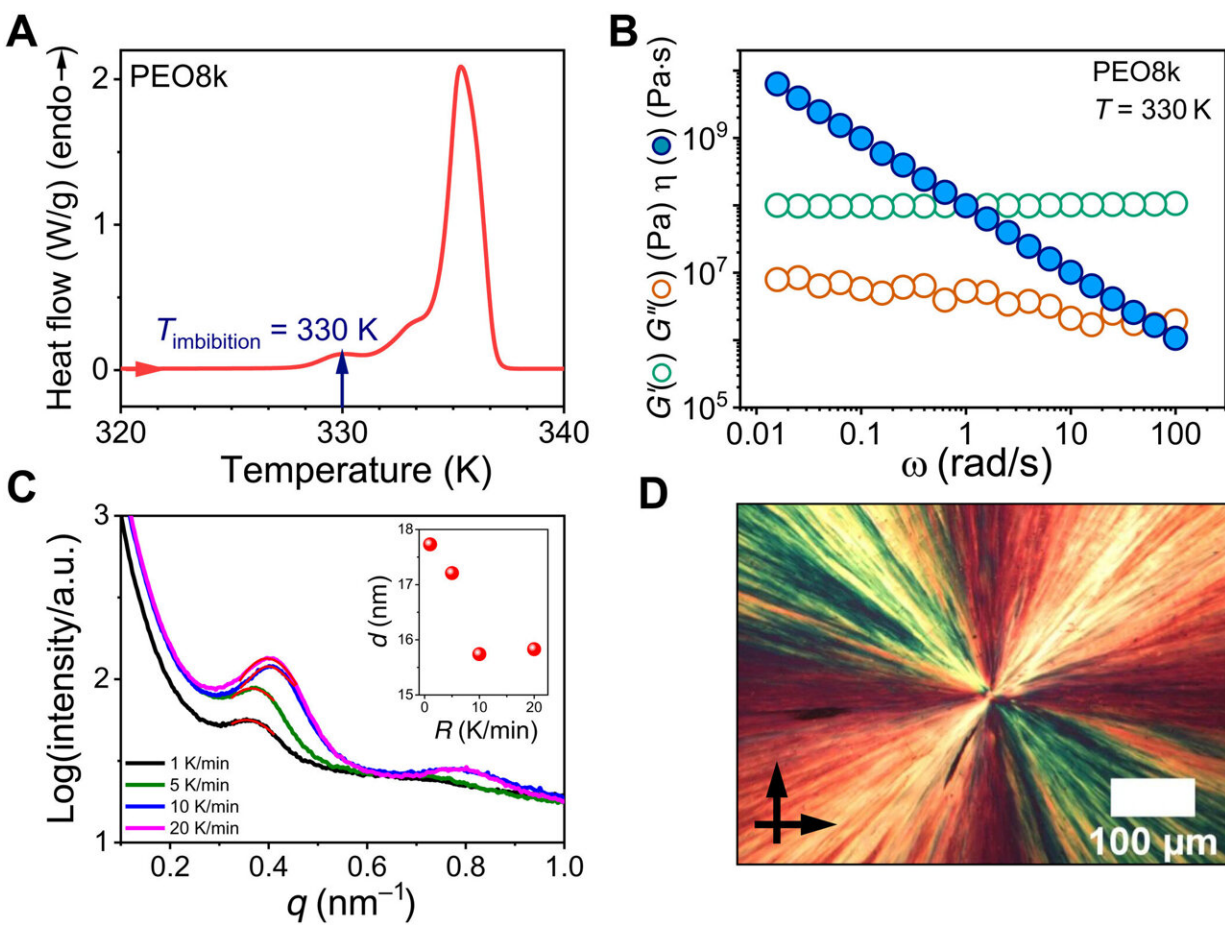


# When crystals flow: Semicrystalline polymer shown to flow at temperatures below its melting point

May 19 2023, by Thamarasee Jeewandara



Bulk PEO8k thermodynamics, rheology, and morphology. (A) Differential scanning calorimetry (DSC) heating curve (rate = 10 K/min) showing (apparent) melting at 335 K. The imbibition temperature ( $T = 330 \text{ K}$ ) is indicated with an arrow. (B) Storage modulus (green circles), loss modulus (red circles), and

viscosity (blue spheres) measured at the imbibition temperature ( $T = 330$  K) measured in rheology. (C) Small-angle x-ray scattering (SAXS) curves of PEO8k obtained at ambient temperature following slow cooling from the melt. The lamellar domain spacing is shown in the inset for different cooling rates,  $R$ , a.u., arbitrary units. (D) Spherulitic morphology obtained by polarizing optical microscopy (POM) with crossed polars at ambient temperature following slow cooling from the melt. Credit: *Science Advances* (2023). DOI: 10.1126/sciadv.adg8865

Semicrystalline polymers are solids that are assumed to flow only above their melting temperature. In a new study published in *Science Advances*, Chien-Hua Tu and a research team at the Max Planck Institute for Polymer Research in Germany and the University of Ioannina Greece confined crystals within nanoscopic cylindrical pores to show the flowing nature of semicrystalline polymers below their melting point, alongside an intermediate state of viscosity to the melt and crystal states.

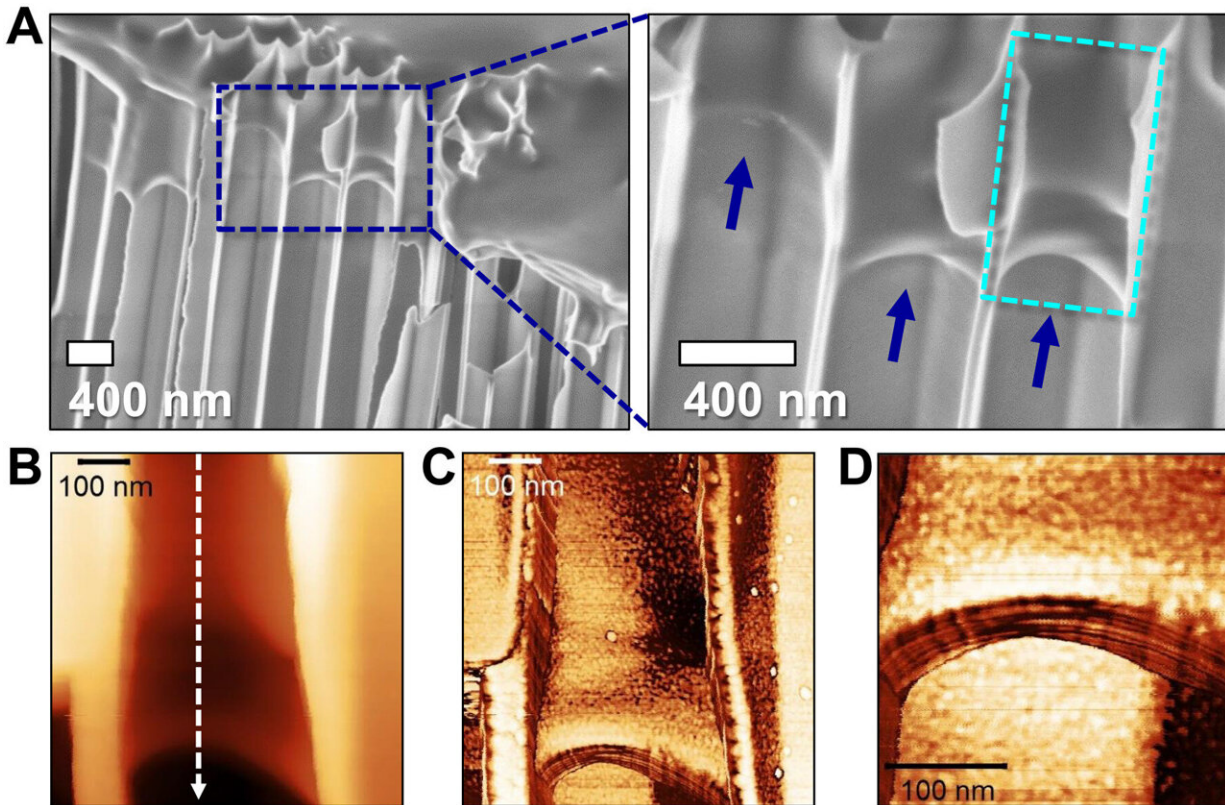
The capillary process was strong during the phenomenon and dragged the [polymer chains](#) into the pores without melting the crystal. The unexpected improvement in flow facilitated [polymer](#) processing conditions applicable to low temperatures, suited for use in organic electronics.

## Crystalline state

About 2,500 years ago, the philosopher Heraclitus proposed that ["everything flows,"](#) and while perfect crystals at zero temperature do not flow, [crystalline materials](#) do flow under specific conditions. For example, existing research [from about 100 years ago](#) showed that the flow of cast iron in the form of flowing metal grains surrounded by a thin amorphous layer is analogous to an undercooled liquid.

Using [molecular dynamics simulations](#), researchers have confirmed the ideas to further suggest the significance of the complex grain boundary "fluid" on plastic deformation. For instance, the inner core of the Earth is similarly proposed to [retain iron in a crystalline state](#). Furthermore, the core of planets such as [Neptune and Uranus](#) are composed of superionic crystalline water, and flow to generate their magnetic field, which may have ultimately led to our own existence.

Crystalline materials that exhibit fluid-like mobilities are known as "[superionics](#)" and are important for energy applications. Semicrystalline polymers are solids that do not flow under normal conditions. In this work, Tu and colleagues showed how even the semicrystalline polymers underwent flow. To examine the phenomenon, they used two semicrystalline polymers; [poly \(ethylene oxide\)](#) and [poly\( \$\epsilon\$ -caprolactone\)](#) with specific molecular characteristics. The [materials scientists](#) developed self-ordered nanoporous alumina templates for the study, based on [existing literature protocols](#).



Imbibition of PEO8k in nanopores revealed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). (A) Left: SEM image from a fractured surface of anodic aluminum oxide (AAO) having nanopores with a diameter of 400 nm infiltrated with PEO8k at 330 K for 28 days. Right: A zoom-in to the blue rectangular dashed area in left. Blue arrows indicate the meniscus. (B) AFM two-dimensional height image corresponding to the cyan rectangular dashed area of (A, right) (C) AFM two-dimensional image to the same area as (B). (D) A zoom-in AFM two-dimensional image to the meniscus region. Credit: *Science Advances* (2023). DOI: 10.1126/sciadv.adg8865

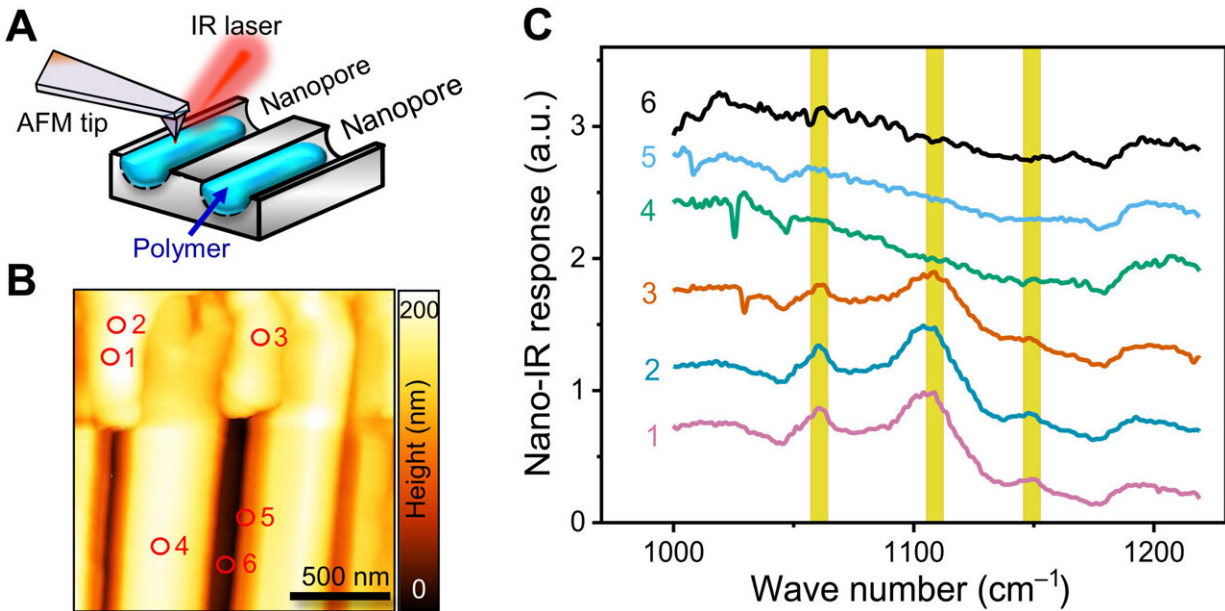
## Materials characterization

The scientists examined the thermodynamics, structural and rheological properties of bulk polyethylene oxide materials. And the data confirmed

the material film on the alumina template to be in a semicrystalline state. The team observed the domain spacing organization of crystalline lamellae with [small-angle X-ray scattering](#). They used [polarizing optical microscopy](#) to study the superstructure of bulk polyethylene oxide with a film slowly cooled from melt to ambient temperature. The outcomes indicated a single spherulitic superstructure for polyethylene oxide, while the structural dynamics of poly( $\epsilon$ -caprolactone) synthesized with a catalyst differed.

The research team carried out a 28-day [imbibition](#) (uptake of water that leads to swelling of materials) of the two polymer materials within anodic aluminum oxide templates and observed the samples with [scanning electron microscopy](#) and [atomic force microscopy](#) to characterize them. In contrast to the relatively smooth appearance of polyethylene oxide, the poly( $\epsilon$ -caprolactone) materials showed abundant grain structures due to diverse morphological origins in intracrystalline diffusion. After studying the surface appearances of materials, the researchers performed [nano-infrared microscopy](#) to obtain additional images of the surface topography of the two materials. The outcomes clearly showed the semicrystalline nature of polyethylene oxide. They also addressed the possibility of the capillary force in the experimental setup to be sufficiently high to melt the crystals during flow and noted the viscosity of semicrystalline polymers to be reduced during the experiments.





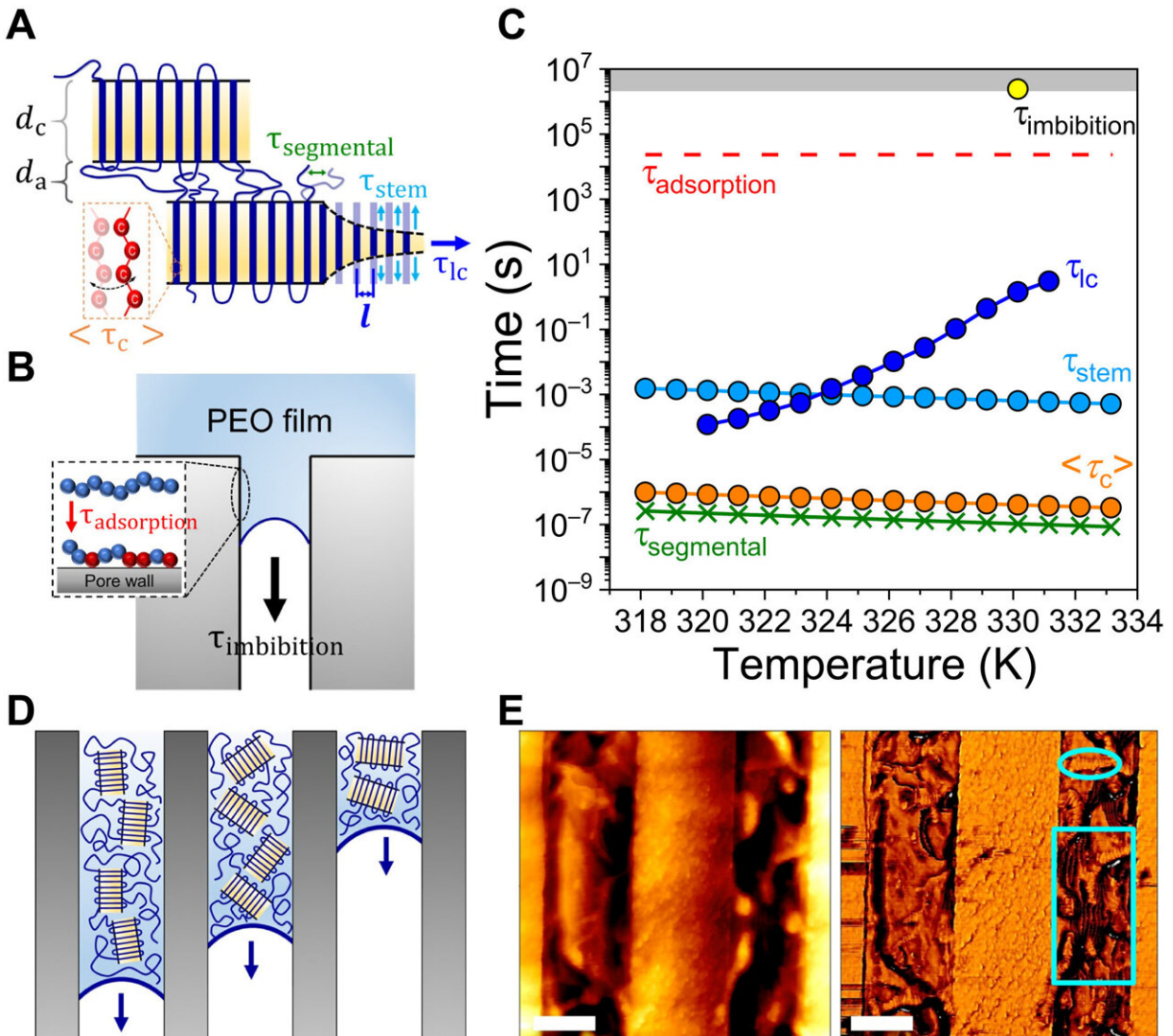
Nano-infrared (IR) reveals the semicrystalline nature of the polymer in the nanopores. (A) Schematic arrangement of the sample for the nano-IR measurements. After scanning the edge of the anodic aluminum oxide (AAO) surface, the atomic force microscopy (AFM) tip is positioned on the polymer or on the AAO surface. Then, the wavelength of the IR laser is tuned. The vibrational amplitude of the AFM tip corresponds to the nano-IR response of the selected position, respectively. (B) Topographic image of the AAO nanoporous sample filled by PEO8k. We selected three positions on the PEO (#1, #2, and #3) and three positions on the AAO (#4, #5, and #6), respectively, and recorded IR spectra. (C) Corresponding IR spectra taken at the marked positions in (B). For positions #1 to #3, absorption peaks at 1061, 1108, and 1149  $\text{cm}^{-1}$  are present (in yellow) that are absent for positions #4 to #6. Peaks at 1061, 1108, and 1149  $\text{cm}^{-1}$  are typical for semicrystalline PEO. Credit: *Science Advances* (2023). DOI: 10.1126/sciadv.adg8865

## Mechanisms of imbibition

The mechanisms of fluid uptake and materials swelling known as imbibition from the semicrystalline state relied on the dynamics of its

crystalline and amorphous domains. Four processes acted on the amorphous and crystalline regions; segmental relaxation governed the dynamics in the amorphous domain, whereas three other processes affected the crystalline domain to demonstrate intracrystalline chain diffusion for crystal-mobile polymers such as polyethylene oxide.

Since the imbibition of crystals also involved the diffusion of entire crystallites, Tu and the team examined the influence of the molar mass of the polymers on the process of imbibition. The outcomes showed that the molar mass regulated the imbibition speed.



Molecular mechanism and associated time scales during imbibition of semicrystalline polymers in nanopores. (A and B) Hierarchical structures and associated kinetics pertinent to semicrystalline polymers: (A) Organization of polymer chains into ordered lamellae involves the movement of segments within the crystalline ( $d_c$ ) and amorphous ( $d_a$ ) regions. Four processes are defined as follows:  $\tau_{\text{stem}}$  represents the diffusion time of PEO chains in the length scale of the crystalline domain ( $d_c$ );  $\tau_{\text{lc}}$  illustrates the growth time of a unit crystal lamellae; depicts the switching time of two helical defect jumps within the crystal;  $\tau_{\text{segmental}}$  represents the segmental dynamics within the amorphous regions.  $l$  represents the intermolecular distance ( $l = l/2$ ;  $a$  and  $b$  are the crystal unit cell parameters along  $x$  and  $y$  axes, respectively). (B) Imbibition of polymer chains ( $\tau_{\text{imbibition}}$ ) proceeds via adsorption with a characteristic time  $\tau_{\text{adsorption}}$ . The anchored units on the pore walls are indicated with the red color. (C) Characteristic time scales and their temperature dependence:  $\tau_{\text{imbibition}}$  (yellow sphere),  $\tau_{\text{adsorption}}$  (red dashed line),  $\tau_{\text{lc}}$  (blue spheres),  $\tau_{\text{stem}}$  (cyan spheres), (orange spheres), and  $\tau_{\text{segmental}}$  (green crosses). The original data are provided in table S1. (D) The effect of lamellar orientation with respect to the pore axes on the variable penetration lengths. (E) AFM height (left) and phase (right) images reveal well-oriented crystalline (PCL) lamellae inside nanopores (cyan framed regions). Scale bars, 200 nm. Credit: *Science Advances* (2023). DOI: 10.1126/sciadv.adg8865

## Outlook

In this way, Chien-Hua Tu and colleagues used several imaging methods in [materials science](#), such as scanning [electron microscopy](#), [atomic force microscopy](#), and nano-infrared results to examine how semicrystalline polymers underwent flow within nanopores made of anodic aluminum oxide via [capillary action](#). They measured the viscoelastic behavior of the polymers with a [shear rheometer](#), and the capillary action appeared to drive the polymer adsorption process.



While successful imbibition was a relatively slow process, the capillary force was strong enough to drag polymer crystallites into the nanopores without melting the crystals. The unexpected increase in flow while preserving the polymer crystallites applied to polymer processing at low temperatures. Such phenomenon can lead to cold flow and subsequent bonding of polymers to ceramics or metal under specific conditions to prevent polymer degradation. Such semicrystalline polymers and [ferroelectric materials](#) have a variety of applications in organic electronics to affect their electronic and physical properties.

**More information:** Chien-Hua Tu et al, When crystals flow, *Science Advances* (2023). [DOI: 10.1126/sciadv.adg8865](https://doi.org/10.1126/sciadv.adg8865)

© 2023 Science X Network

Citation: When crystals flow: Semicrystalline polymer shown to flow at temperatures below its melting point (2023, May 19) retrieved 23 April 2024 from <https://phys.org/news/2023-05-crystals-semicrystalline-polymer-shown-temperatures.html>

This document is subject to copyright. Apart from any fair dealing for the purpose of private study or research, no part may be reproduced without the written permission. The content is provided for information purposes only.