



# Molecular Breathing Room

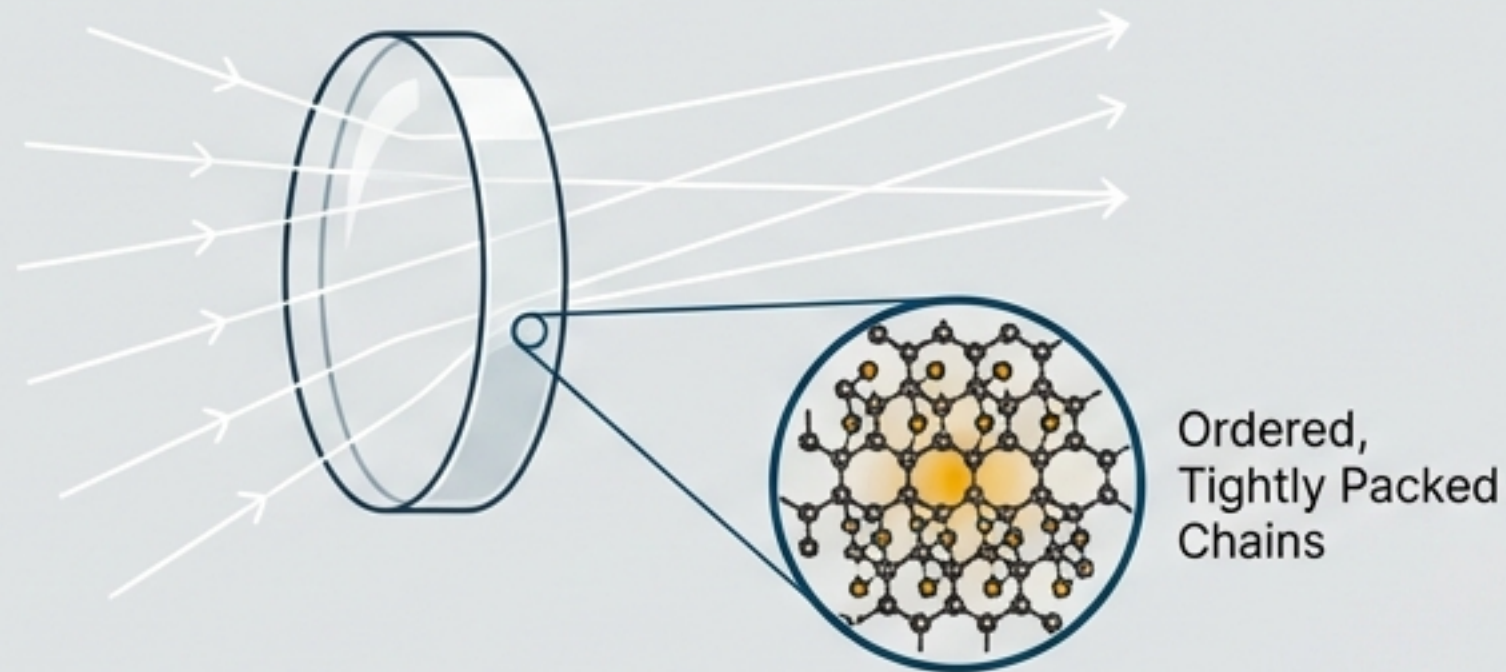
An Introduction to **Glass Transition**, **Free Volume**, and **Plasticization** in Polymers



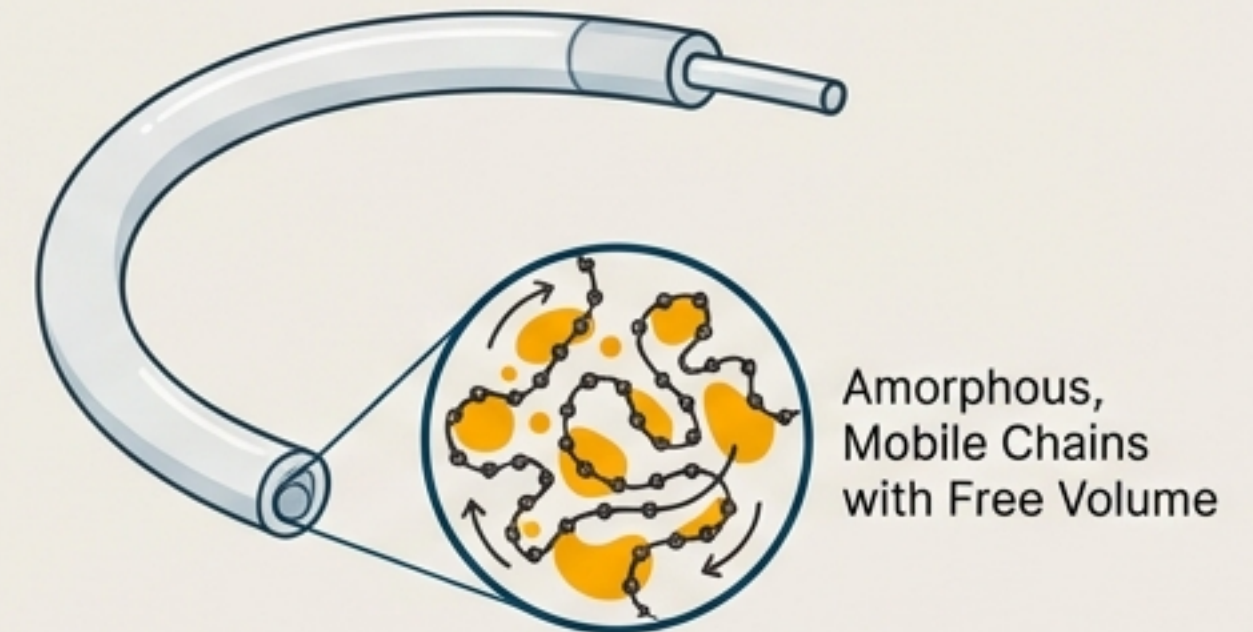
# Polymers exist in two worlds: the rigid glass and the flexible rubber.

The performance of a polymer is dictated by its state. Below a critical temperature, it is a stiff, brittle glass. Above it, a soft, deformable rubber. The transition between these states governs the success or failure of materials in critical applications.

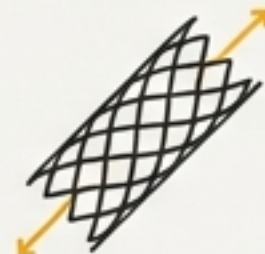
## The Rigid Glass



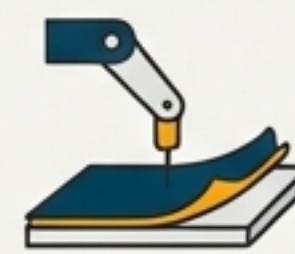
## The Flexible Rubber



Advanced  
Packaging



Biomedical  
Devices



Protective  
Coatings

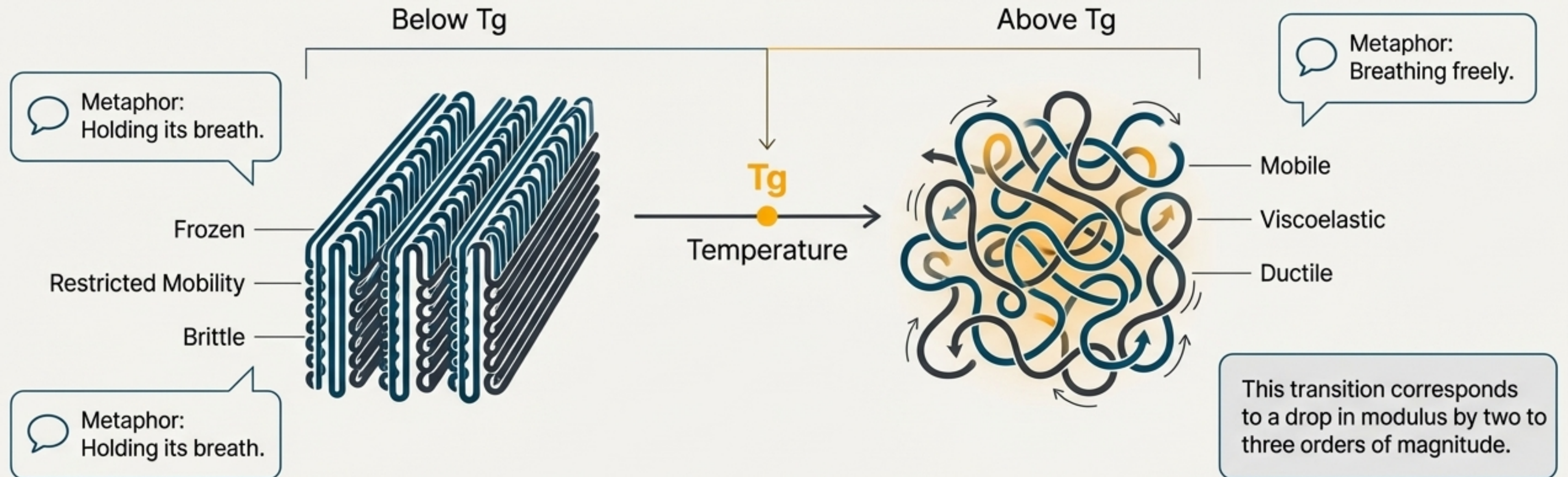


3D-Printed  
Components



# The glass transition ( $T_g$ ) is the point where molecular chains begin to breathe.

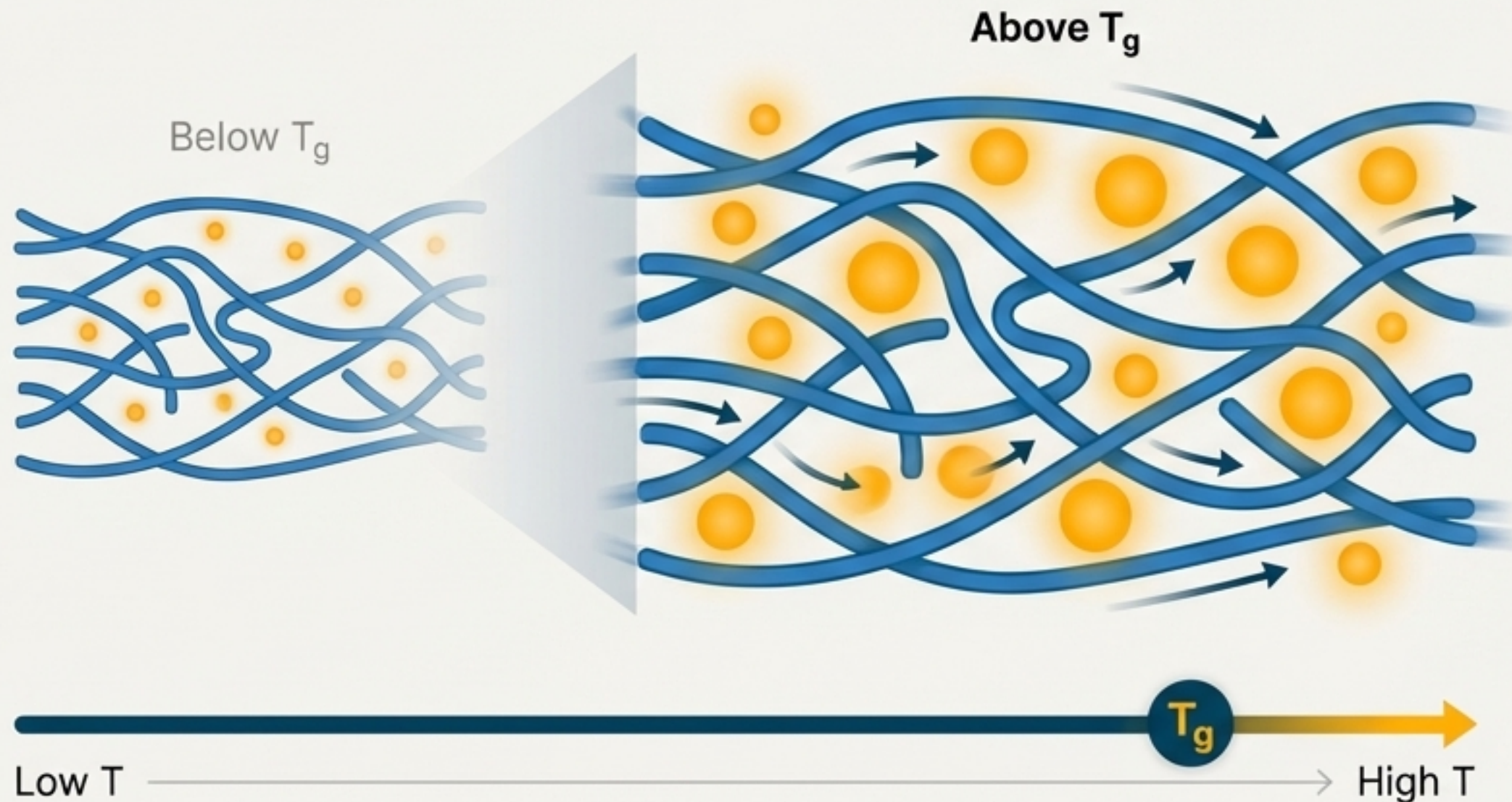
Unlike a sharp melting point,  $T_g$  is a kinetic phenomenon—a temperature range where long-range cooperative motion among polymer chain segments becomes activated. This unlocks a dramatic change in material properties.





# Free volume is the empty space that enables molecular movement.

Free-volume theory provides a molecular model for the changes at  $T_g$ . It is the microscopic, unoccupied volume within the polymer that allows segments to rearrange. As temperature rises, this volume expands, creating the “breathing room” needed for chains to become mobile.



Free volume fraction at a given temperature.

Linear expansion of free volume above  $T_g$

$$f(T) = f_0 + \alpha(T - T_g)$$

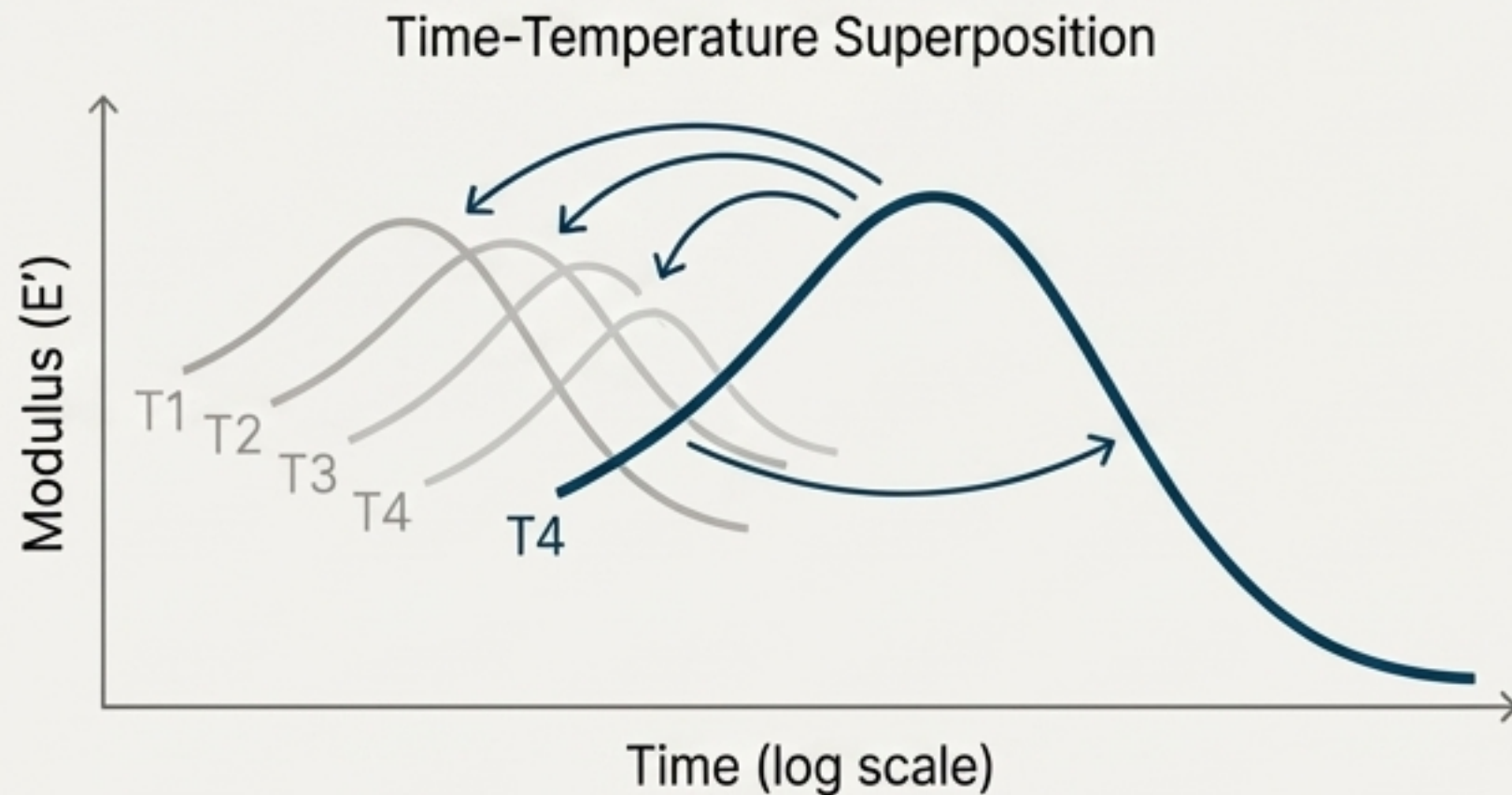
Free volume at  $T_g$



# This 'breathing room' can be modeled, and it changes over time.

## Predicting Relaxation (WLF Equation)

The Williams–Landel–Ferry (WLF) equation is a powerful tool that models the temperature-dependent relaxation of polymers near  $T_g$ . It underpins time-temperature superposition (TTS) for creating viscoelastic master curves.



Williams, Landel & Ferry (1955)

## The Slow Stiffening of Glass (Physical Aging)

Below  $T_g$ , the polymer is not in equilibrium. It slowly relaxes, and its free volume gradually decreases over time. This “physical aging” causes the material to become progressively stiffer and more brittle.



**Implication:** Critical for the long-term dimensional stability of optical lenses, medical parts, and barrier films.

Struik (1978)

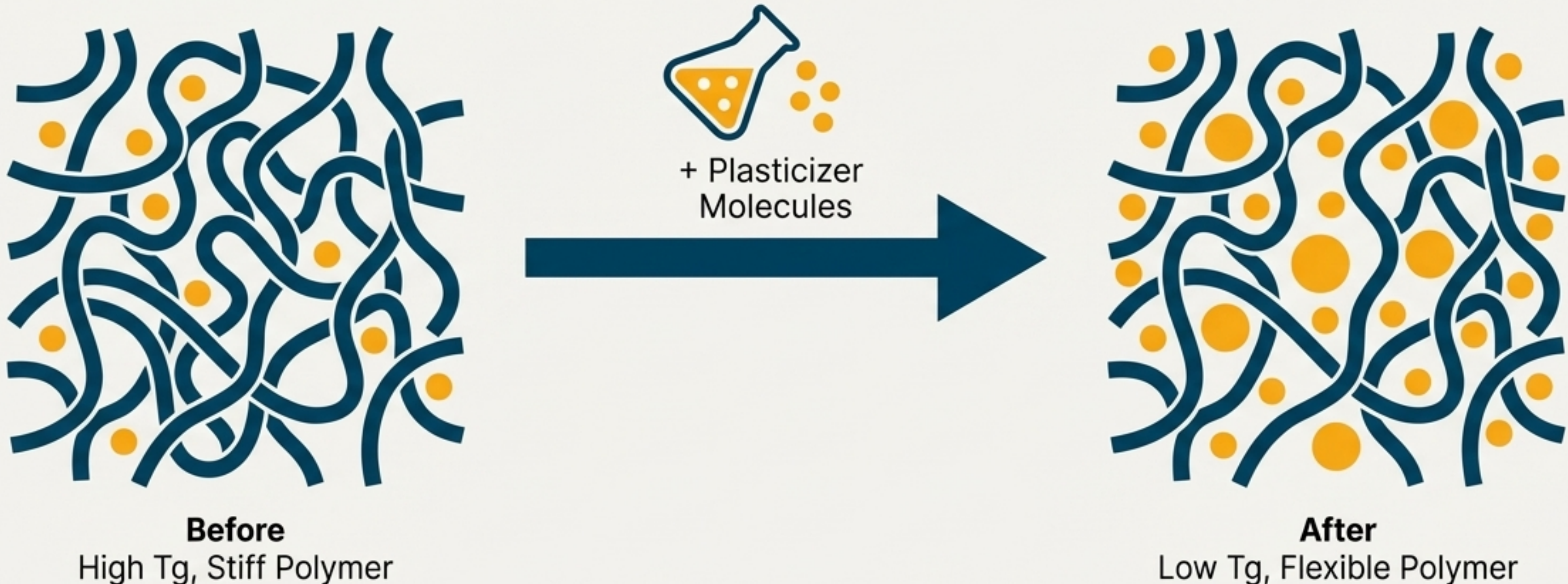


# Plasticization: The deliberate or accidental creation of molecular breathing room.

Plasticizers are small molecules that infiltrate the polymer matrix. By inserting themselves between chains, they **increase free volume** and/or weaken intermolecular attractions.

## The Result

- The glass transition temperature ( $T_g$ ) is lowered.
- The material becomes softer and more flexible.





# Plasticization occurs through three distinct mechanisms.



## External Plasticization

Small molecules are intentionally blended into the polymer. They are not chemically bonded.

### Mechanism:

Physically separate chains, reducing cohesive energy.

### Example:

Phthalates or citrates added to PVC to make it flexible.

Sears & Darby (1982)



## Internal Plasticization

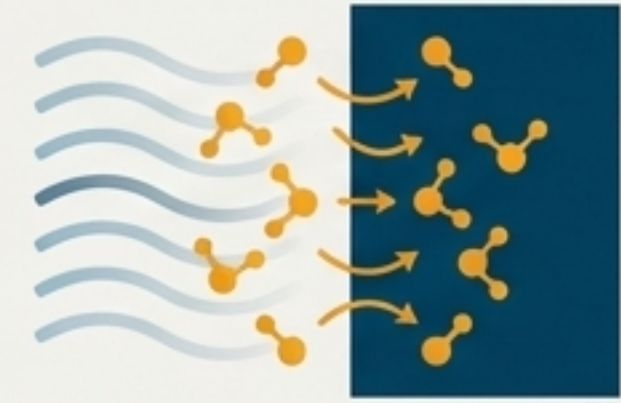
Flexibility is permanently built into the polymer's chemical structure.

### Mechanism:

Copolymerization with flexible monomers or adding long, soft side chains.

### Example:

Creating a copolymer with built-in "hinges."



## Environmental Plasticization (SIP)

Small molecules from the environment (e.g., water, solvents) diffuse into the polymer.

### Mechanism:

Unintentionally increases free volume, temporarily softening the material.

### Example:

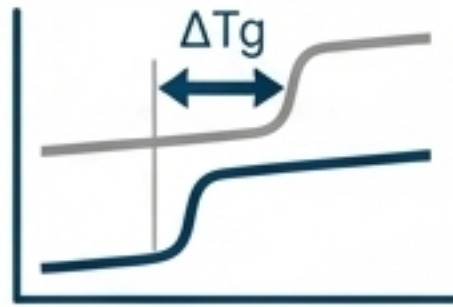
Humidity affecting epoxy resins; solvent exposure weakening PMMA.



# Increasing molecular mobility changes everything.

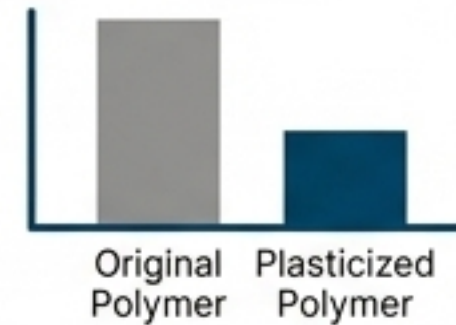
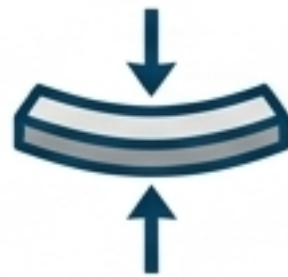
Plasticization has profound and measurable effects on a polymer's thermal and mechanical properties.

## Lower T<sub>g</sub>



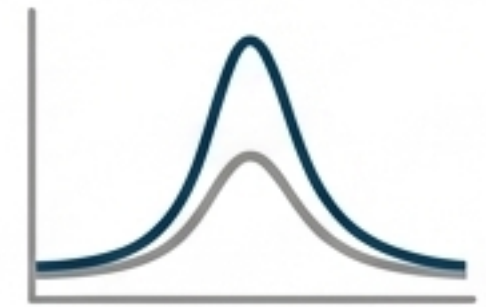
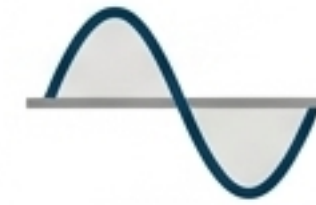
The heat-capacity step in a DSC scan shifts to a lower temperature.

## Reduced Modulus



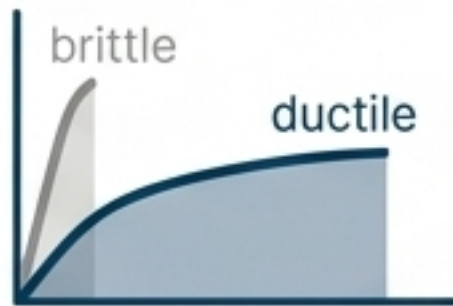
The material becomes less stiff, especially near its transition temperature.

## Increased Damping



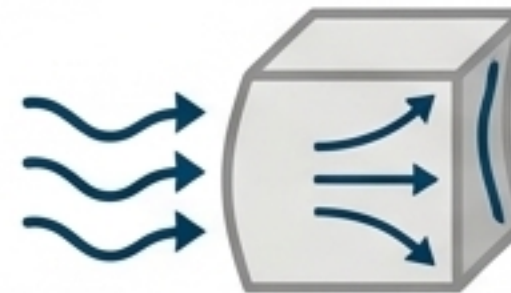
The  $\tan \delta$  peak in a DMA scan becomes higher and may shift.

## Greater Ductility



The polymer can stretch more before breaking, increasing toughness.

## Dimensional Instability

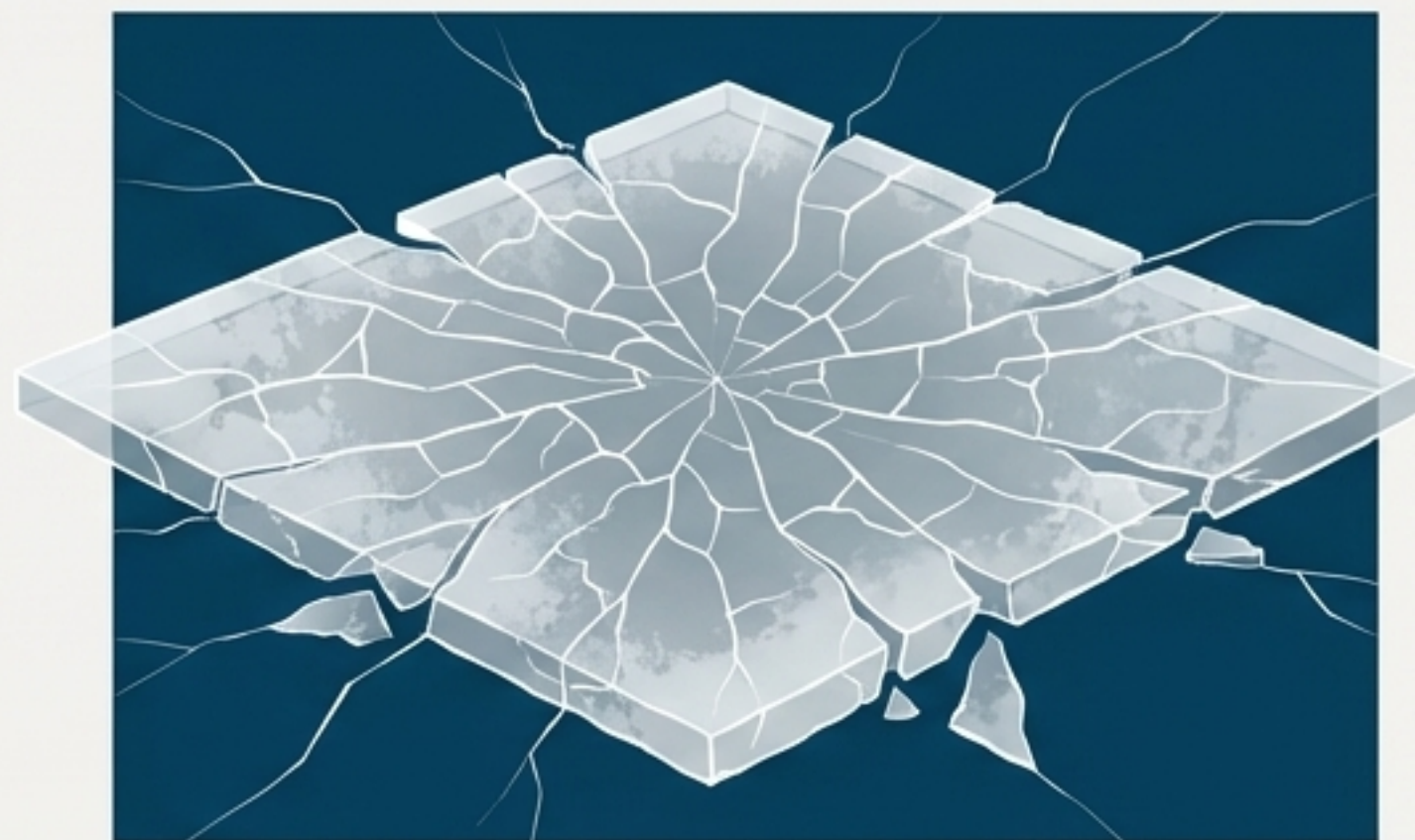
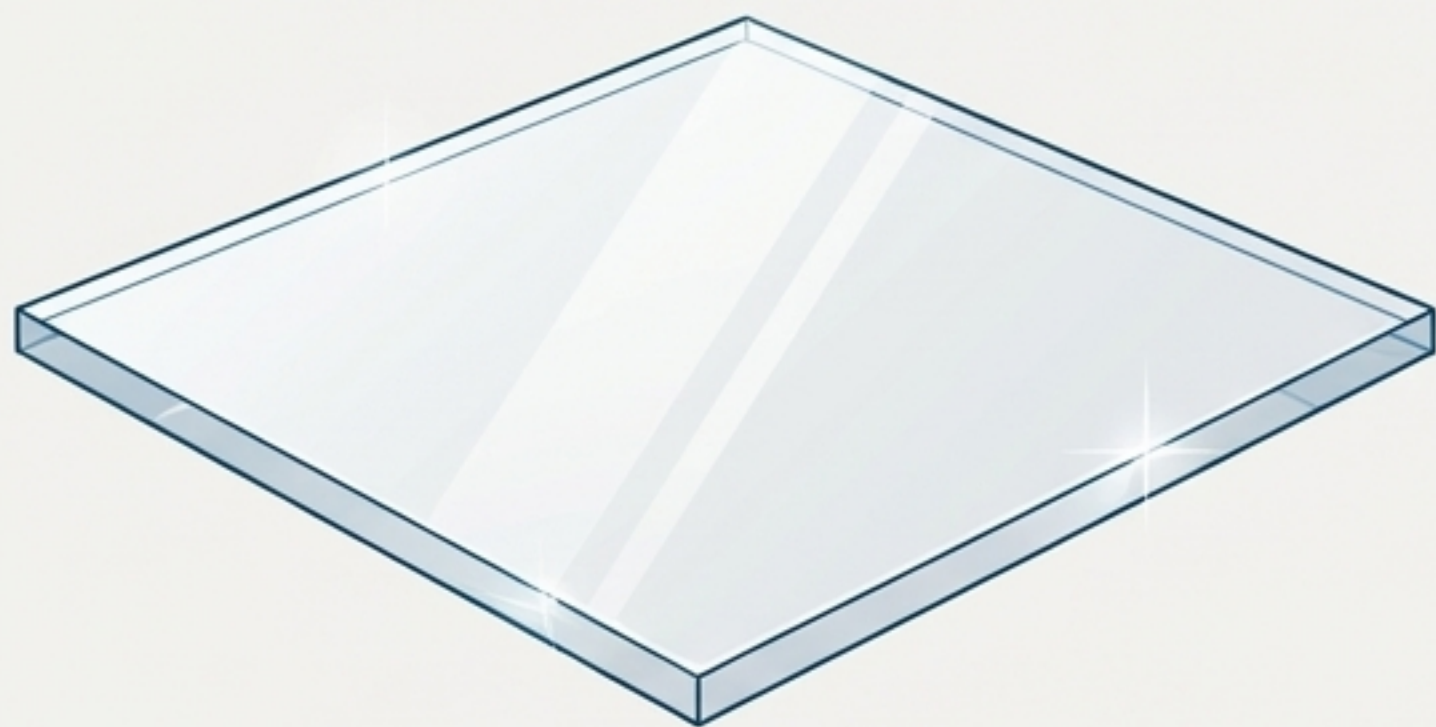


Non-uniform plasticization can cause warping, swelling, and internal stress.



# Case Study: The Mysterious Degradation of PMMA

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## The Subject

Poly(methyl methacrylate), or **PMMA**. A widely used thermoplastic known for its rigidity and optical clarity. We think of it as a stable, durable glass. ( $T_g \approx 105\text{ }^{\circ}\text{C}$ ).

## The Mystery

When exposed to common solvents like alcohol, this “invincible” material mysteriously **whitens, cracks, and loses its structural integrity**. Why?

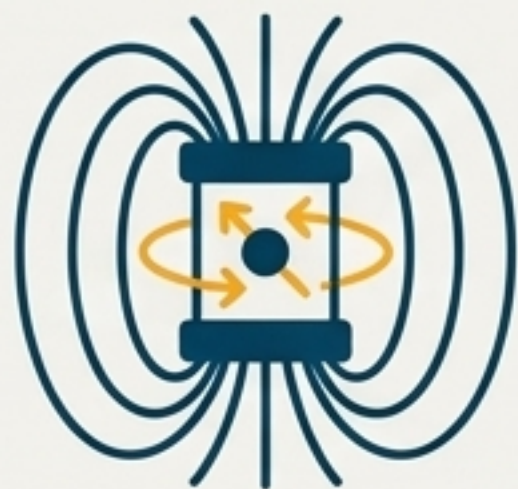
## The Investigation

We will follow the 2023 study by Kavda, Golfomitsou, & Richardson, who used a suite of advanced techniques to solve this puzzle.



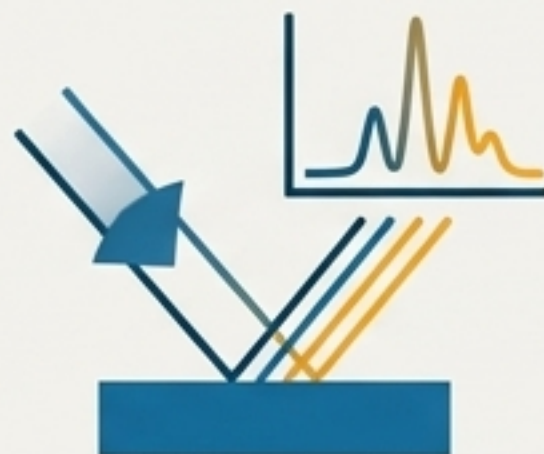
# A multi-pronged investigation to uncover the truth.

To understand the changes happening inside the PMMA, Kavda et al. used a combination of complementary characterization techniques.



## Unilateral NMR

To quantify how much solvent was absorbed and to directly measure changes in molecular mobility inside the polymer.



## ATR-FTIR Spectroscopy

To detect changes in the local chemical environment, revealing how solvent molecules were interacting with the PMMA chains.



## Mass Change Tracking

To determine the kinetics of solvent absorption and swelling.



## Optical Examination

To document the macroscopic evidence of damage—microcracks, whitening, and surface roughness.



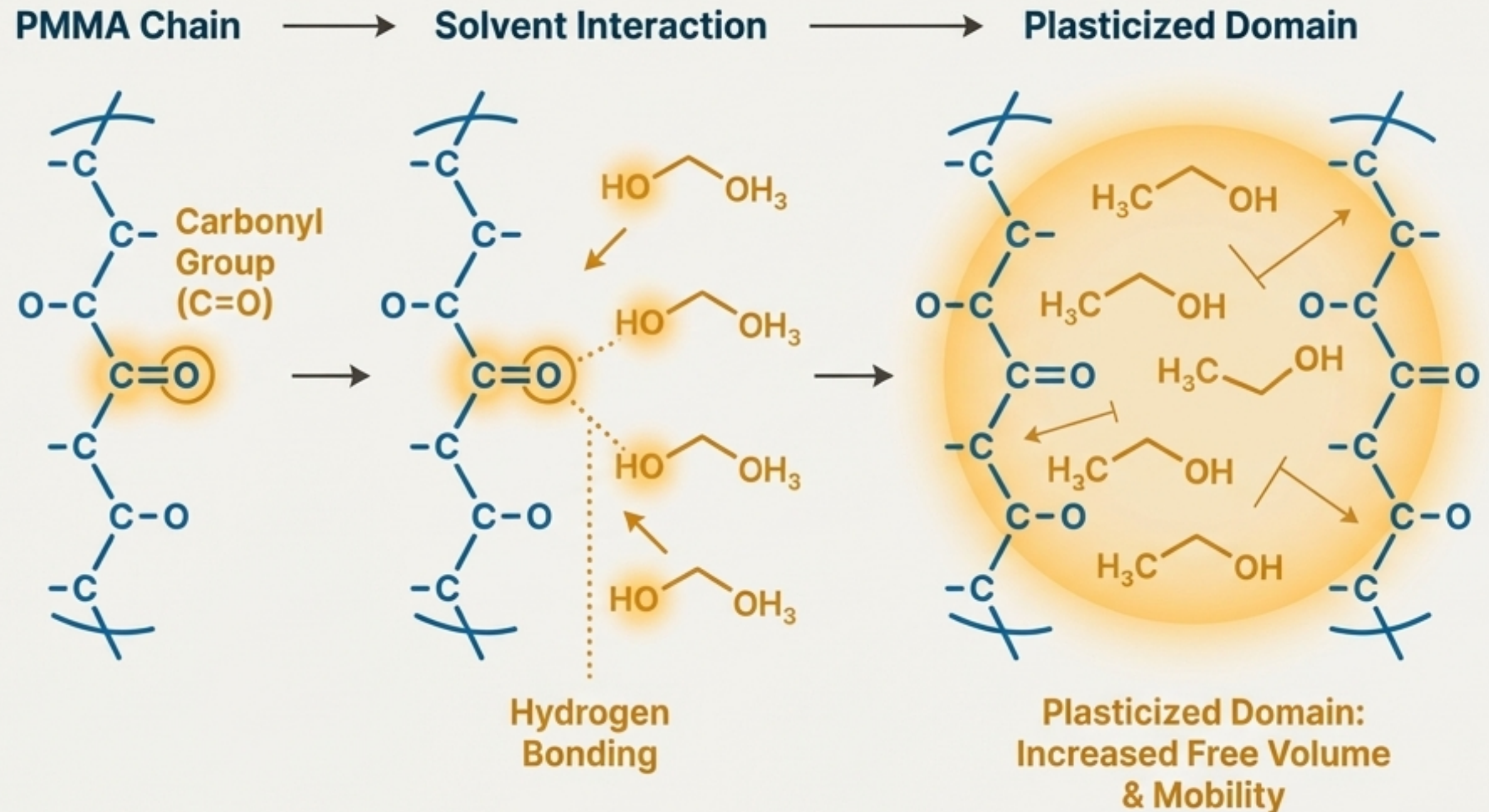
# Clue #1: Polar solvents forced their way in, creating plasticized domains.

## The Finding

The study found a profound difference in solvent uptake. Polar solvents (ethanol, water) permeated deeply and rapidly. Nonpolar petroleum ether showed negligible absorption.

## The Reason

Polar solvents have a strong affinity for the carbonyl (C=O) groups in PMMA. They form hydrogen bonds, allowing them to wedge between polymer chains and create new free volume.





## Clue #2: Chemical fingerprints reveal a disruption of molecular forces.

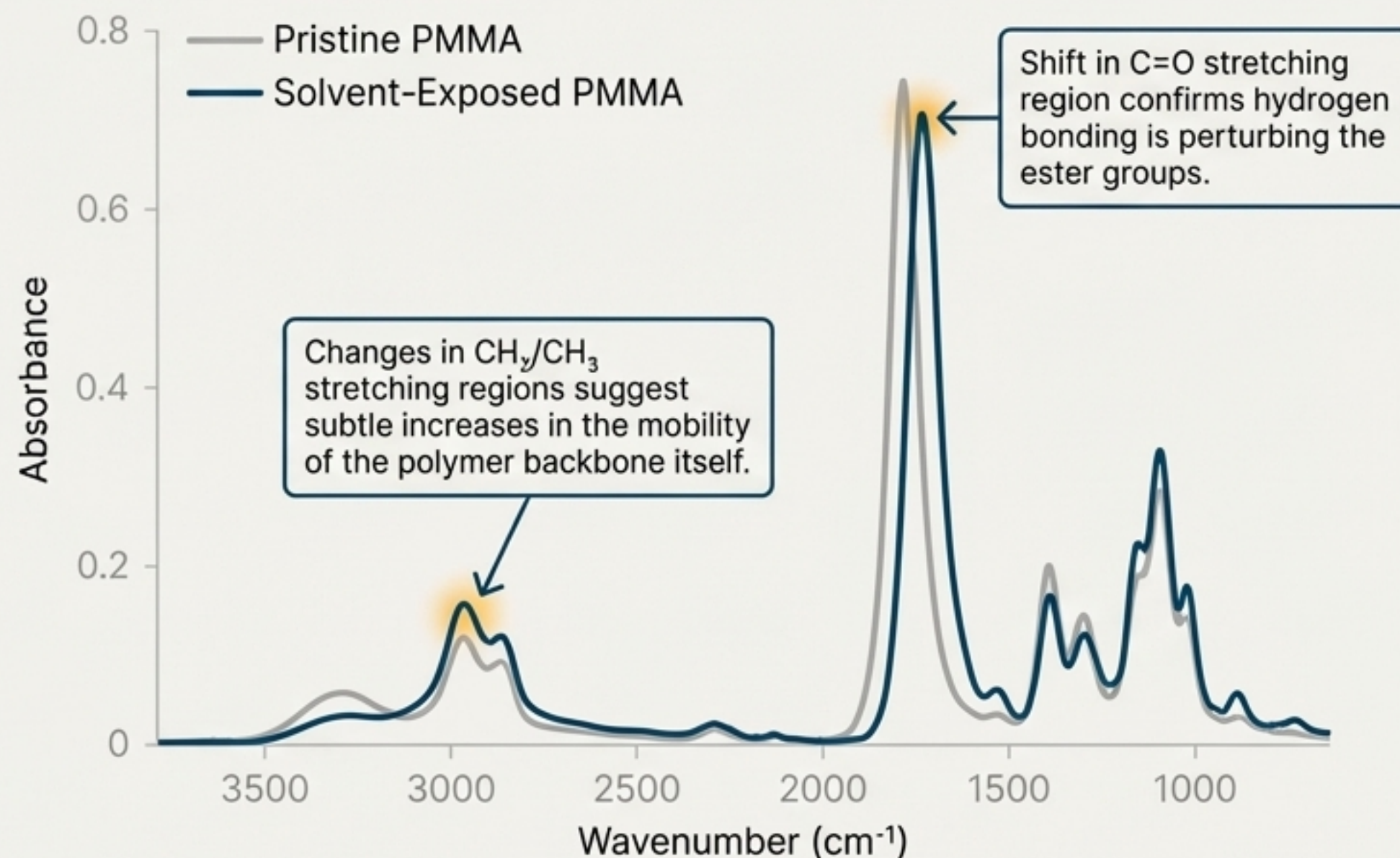
**The Finding:** ATR-FTIR spectra showed noticeable shifts after solvent exposure, providing direct evidence of molecular interactions.

### The Evidence

- **Shift in C=O stretching region:** Confirmed that the solvent's hydrogen bonding was perturbing the environment around the ester groups.
- **Changes in CH<sub>2</sub>/CH<sub>3</sub> stretching regions:** Suggested subtle increases in the mobility of the polymer backbone itself.

### The Connection

Weakening these intermolecular forces lowers the energy needed for segmental motion. This is a classic mechanism for depressing  $T_g$  and is strong evidence for plasticization.

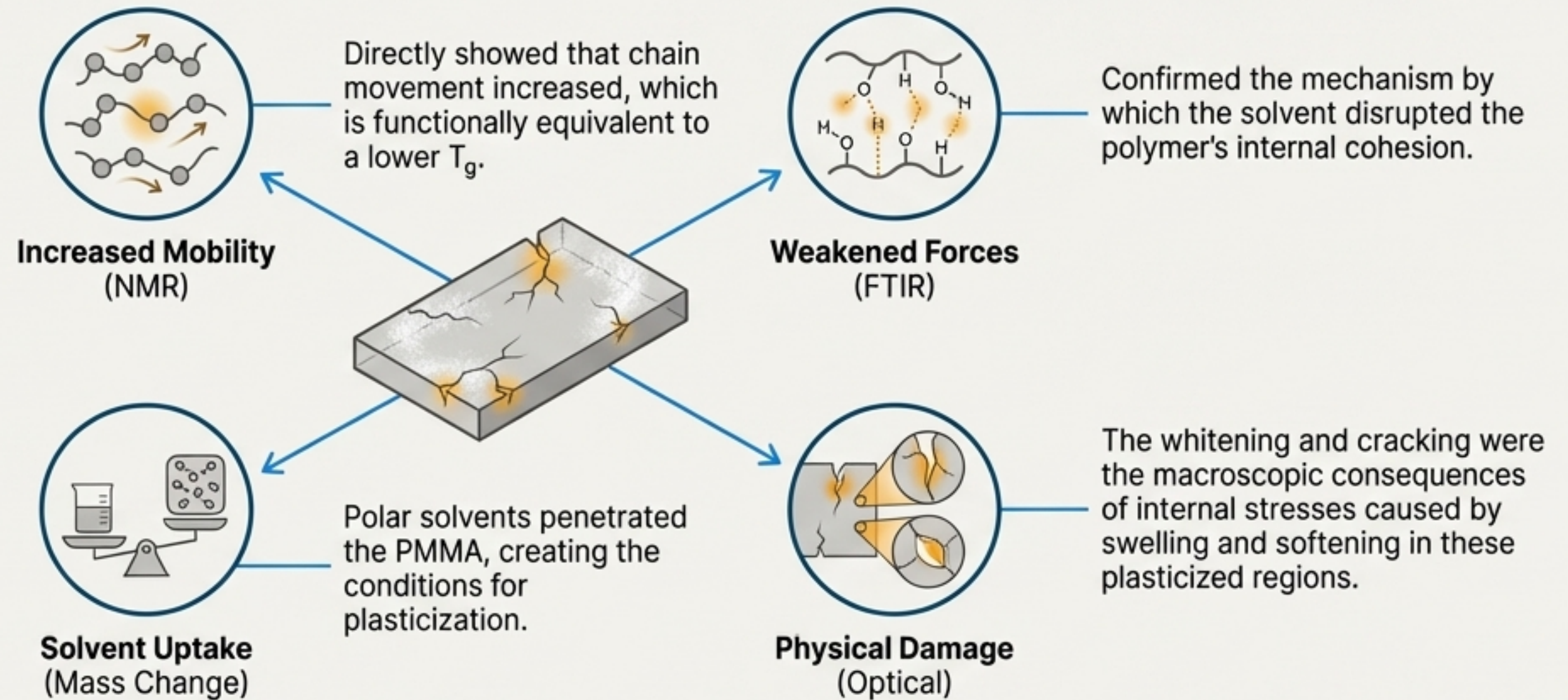




# The verdict is in: Environmental plasticization is the culprit.

## Synthesizing the Evidence

- Directly showed that chain movement increased, which is functionally equivalent to a lower  $T_g$ .
- Confirmed the mechanism by which the solvent disrupted the polymer's internal cohesion.
- Polar solvents penetrated the PMMA, creating the conditions for plasticization.



The solvent acted as a classic environmental plasticizer, dramatically increasing free volume and lowering the effective  $T_g$  of the PMMA, leading to its mechanical failure.

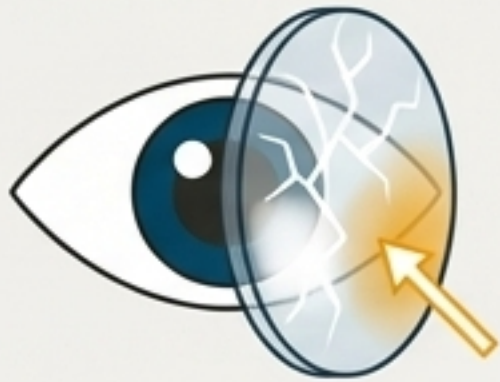


# The consequences are lasting and have serious engineering implications.

The study also showed that the solvent's effect can permanently alter the polymer's structure. By erasing the material's physical aging history (as described by Struik), solvent exposure resets the clock on long-term relaxation behavior.

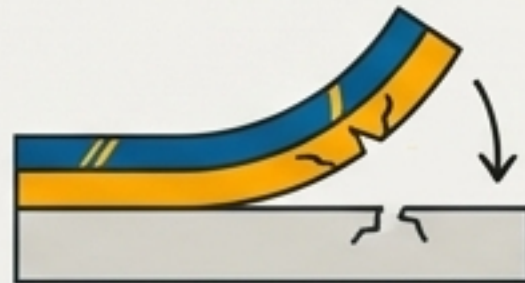
## Key Takeaways for Application Design

### Optical Devices



Solvent-induced whitening or cracking can destroy transparency and performance in PMMA lenses.

### Adhesives & Coatings



Exposure to cleaning solvents can reduce stiffness and lead to premature failure.

### 3D-Printed Parts



Residual solvents from post-processing can act as unintended plasticizers, altering final mechanical properties.

### Cultural Heritage



PMMA-based artifacts are at risk of degradation in humid or polluted environments.



# Mastering polymer design means mastering the molecular environment.

1. The **Glass Transition ( $T_g$ )** is the fundamental switch governing a polymer's state from rigid glass to flexible rubber.
2. **Free Volume**—the “molecular breathing room”—is the underlying mechanism that dictates chain mobility and controls the  $T_g$ .
3. **Plasticization**, whether intentional or environmental, directly manipulates free volume, altering a polymer's properties for better or worse.

A deep understanding of these interconnected principles is not just academic; it is essential for designing and deploying polymer systems that are durable, stable, and reliable in the real world.

