Amorphous Organic Solids and Their Crystallization

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Organic glasses have special applications

Drug delivery
Glasses are more soluble than crystals

Food

Bio-preservation

In sugar glasses

In amber
From yesterday’s workshop

- Glasses (amorphous solids) are made by cooling liquids, as well as by including milling, drying hydrates, vapor deposition, …

- Solidity does not mean no mobility.
  - Glasses relax
  - Glasses can crystallize

This talk

(1) Engineering organic glasses

(2) Crystal growth in organic glasses – bulk

(3) Crystal growth in organic glasses – surface
A glass is a “living thing” – it relaxes over time

Can a glass be made at such a low energy that virtually no relaxation occurs on storage?

Heat capacity of OTP glass annealed for up to 10 hrs at 233 K ($T_g - 13$ K). Longer annealing leads to lower energy and higher “heat of melting”.


Vapor deposition can produce stable glasses

VD glasses can be 14 J/g lower in energy than ordinary glasses – a level reached only after very long aging (perhaps $10^6$ years)

Glasses are generally isotropic, but anisotropy can be introduced by cooling liquids in E field


Vapor deposition can yield anisotropic glasses

**XRD**

**Ellipsometry**

\[ \text{Asymmetric scattering indicates “layered” structure} \]

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Chemistry for Everyone

Glass Doesn’t Flow and Doesn’t Crystallize and It Isn’t a Liquid

Stephen J. Hawkes  


But glasses do crystallize!

Amorphous indomethacin crystallizes in days →

Well known kinetic pattern of crystal growth in one-component liquids

The pattern was predicted by Wilson and Frenkel

A new, fast growth mode emerges near $T_g$

• First observed for OTP by Greet and Turnbull in 1967
• Studied by Oguni and coworkers since 1995
• Unknown for inorganic and polymeric glass formers
Many organic liquids show emergence of GC growth near $T_g$


Two substances not showing GC growth

Nascimento & Zanotto 2010
Studying crystal growth with polymorphs: From the same liquid/glass, which polymorph grows, and which does not?

Some ROY polymorphs show GC growth; some do not.

Polymorphs that grow in glasses are more isotropically packed and “liquid-like”

- **No GC growth**
- **Radial distribution functions**
- **GC growth**

Explanations for GC growth – still imperfect

- **\( \beta \) relaxation.** But the \( \beta \) process is absent in ROY and aged away in OTP (Hikima et al. 1995; Sun et al. 2008)

- **Cluster growth.** But has difficulty explaining the abrupt onset, termination (Hikima et al. 1995)

- **Tension from densification.** But fibers grow rapidly above \( T_g \); no “autocatalysis” (Konishi & Tanaka 2007)

- **Solid-state transition similar to polymorphic conversion and grain-boundary migration.** But no predictive power (Sun et al. 2008)
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“Whereas in many metallic glasses nucleation has been observed to be enhanced at the surface, growth rates are usually quite comparable with those in the bulk.” Koster (Mat. Sci. & Eng. 1988, 97, 233)

[For silicate glasses.] “The crystal growth velocities of crystals in the volume and of the surface layer in the glass volume, as well as of isolated crystals on the glass surface are equal.” Diaz-Mora et al. (J. Non-Crystalline Solids 2000, 273, 81)
Organic glasses can grow crystals faster at the surface than in the bulk


What do surface crystals look like?

α IMC crystals at $T_g - 2^\circ$C

Surface crystals rise above glass surface by 100 – 1000 nm, as they grow laterally

Ye Sun et al. PNAS 2011, 108, 5990
Surface crystals are so thin that they diffract weakly. Can we do better with GADDS?

Effect of PVP on crystal growth in NIF glasses

Ting Cai et al. Pharm. Res. 2011, 28, 2458
Polymer dopants can strongly inhibit bulk crystal growth, but their effect on surface growth is less. Crystal growth in NIF glass at $T_n - 12^\circ C$.


Surface crystallization can be inhibited with a nanocoating.

Wu, Sun, Li, de Villiers, and Yu. *Langmuir* 2007, 23, 5148
Explanations for fast surface crystal growth

- *Tension from crystal growth is relaxed at surfaces* (Schmelzer 1993)

- *Surface mobility and opportunity for upward growth* (Sun et al. 2011)

The latter model better explains inhibition by nanocoating and upward growth of surface crystals.

Tension-release model tested with polymorphs

Surface diffusion is fast on IMC glasses


Summary

- XRD plays a key role in studying amorphous solids and glasses
- Organic glasses can be “engineered” into have different structures and properties
- Organic liquids develop fast modes of crystal growth as they solidify to glasses in the bulk at the surface
- The phenomena are unknown or uncommon for non-organic glasses