Amorphous Organic Solids and Their Crystallization

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With thanks to: NSF, Abbott, PRF, AstraZeneca

Organic glasses have special applications



This document was presented at PPXRD -Pharmaceutical Powder X-ray Diffraction Symposium

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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



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".

Xi, H.; Sun, Y.; Yu, L. J. Chem. Phys. 2009, 130, 094508.

Vapor deposition can produce stable glasses



Swallen, Ediger, et al. *Science* **2007**, *315*, 353 Zhu & Yu *Chem. Phys. Lett.* **2010**, *499*, 62

VD glasses can be 14 J/g lower in energy than ordinary glasses – a level reached only after very long aging (perhaps 10⁶ years)





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Chemistry for Everyone

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

Stephen J. Hawkes

J. Chem. Educ. 2000, 77, 846

But glasses do crystallize!

Amorphous indomethacin crystallizes in days \rightarrow



Yoshioka et al. J. Pharm. Sci. 1994, 83, 1700







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



Y. Sun et al. *J. Phys. Chem. B* **2008** L. Yu. *Acc. Chem. Res.* **2010**





Explanations for GC growth – still imperfect

• β relaxation. But the β 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)

glass S" crystal (denser)

• 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)





Effect of PVP on crystal growth in NIF glasses





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





Gunn, E.; Guzei, I. A.; Yu, L. Cryst. Growth Des. 2011, 11, 3979-3984



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