

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/5444398>

Crystallization near Glass Transition: Transition from Diffusion-Controlled to Diffusionless Crystal Growth Studied with Seven Polymorphs

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · JUNE 2008

Impact Factor: 3.3 · DOI: 10.1021/jp7120577 · Source: PubMed

CITATIONS

57

READS

27

5 AUTHORS, INCLUDING:



Shuang Chen

AbbVie

7 PUBLICATIONS 304 CITATIONS

SEE PROFILE



Lian Yu

University of Wisconsin–Madison

96 PUBLICATIONS 4,099 CITATIONS

SEE PROFILE

Crystallization near Glass Transition: Transition from Diffusion-Controlled to Diffusionless Crystal Growth Studied with Seven Polymorphs

Ye Sun,[†] Hanmi Xi,[‡] Shuang Chen,^{‡,§} M. D. Ediger,[†] and Lian Yu^{*,†,‡}

Department of Chemistry, University of Wisconsin – Madison, Madison, Wisconsin 53706, and School of Pharmacy, University of Wisconsin – Madison, Madison, Wisconsin 53705

Received: December 24, 2007; In Final Form: February 12, 2008

A remarkable property of certain glass-forming liquids is that a fast mode of crystal growth is activated near the glass transition temperature T_g and continues in the glassy state. This growth mode, termed GC (glass-crystal), is so fast that it is not limited by molecular diffusion in the bulk liquid. We have studied the GC mode by growing seven polymorphs from the liquid of ROY, currently the top system for the number of coexisting polymorphs of known structures. Some polymorphs did not show GC growth, while others did, with the latter having higher density and more isotropic molecular packing. The polymorphs not showing GC growth grew as compact spherulites at all temperatures; their growth rates near T_g decreased smoothly with falling temperature. The polymorphs showing GC growth changed growth morphologies with temperature, from faceted single crystals near the melting points, to fiber-like crystals near T_g , and to compact spherulites in the GC mode; in the GC mode, they grew at rates 3–4 orders of magnitude faster with activation energies 2-fold smaller than the polymorphs not showing GC growth. The GC mode had rates and activation energies similar to those of a polymorphic transformation observed near T_g . The GC mode was disrupted by the onset of the liquid's structural relaxation but could persist well above T_g (up to $1.15 T_g$) in the form of fast-growing fibers. We consider various explanations for the GC mode and suggest that it is solid-state transformation enabled by local molecular motions native to the glassy state and disrupted by the liquid's structural relaxation (the α process).

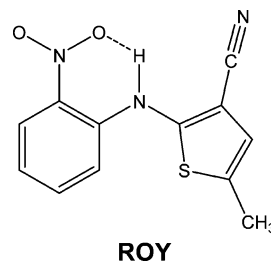
Introduction

The rate of crystal growth from a one-component liquid typically increases and then decreases with supercooling. At small supercooling, the growth rate is limited by the thermodynamic driving force for crystallization, while at large supercooling, the growth rate is limited by molecular diffusion in the liquid.^{1–5} The existence of diffusion-controlled crystal growth is evident from the proportionality of crystal growth rate and diffusivity, $u \propto D$, observed at large enough supercooling.⁴

Diffusion-controlled crystal growth serves as a reference point for a different mode of crystal growth that is activated near the glass transition temperature T_g . For *o*-terphenyl, for example, $u \propto D$ holds over a wide range of temperature in which u changes by 4 orders of magnitude,⁴ but cooling the liquid near T_g causes an abrupt increase of growth rate by 10^3 – 10^4 -fold relative to the diffusion-controlled growth.^{6,7} This phenomenon was apparently first noted by Greet and Turnbull in 1967⁶ and then studied systematically by Oguni and co-workers since 1995.⁷ We shall refer to the new mode of crystal growth as GC (glass-crystal) for it is observable deep in the glassy state. Because its onset is not accompanied by an increase in diffusivity,⁴ the GC mode is reasonably called diffusionless, in contrast to diffusion-controlled growth.

Besides *o*-terphenyl, the GC mode has been observed in several other liquids,^{8–10} all of which are organic glass formers.

The study of the ROY system, in particular, revealed a new feature of GC growth:¹⁰ despite its abrupt onset near T_g to yield space-filling spherulites, the GC mode persists well above T_g (up to $1.15 T_g$ for ROY) in the form of fast-growing fibers.



The GC mode is not anticipated by current theories of crystal growth,¹¹ which assume that diffusion defines the kinetic barrier to crystal growth. The activation of the GC mode marks a transition from diffusion-controlled to diffusionless crystal growth. To our knowledge, this transition has been observed only in organic glass formers, although fast crystal growth is known in inorganic glasses (e.g., amorphous silicon¹² and metallic glasses¹³). The GC mode is important for understanding the stability of amorphous (glassy) materials against crystallization and especially the stability of amorphous drugs, which are often stored and used near T_g .

Oguni and co-workers describe GC growth as the coalescence of homogeneous crystal nuclei, not individual molecules, onto existing crystal surfaces ("homogeneous-nucleation-based crystallization").⁷ They attribute its fast rate to enhanced nucleation near T_g and the control of the process by a secondary relaxation

* Corresponding author. Tel.: (608)263-2263. E-mail: lyu@pharmacy.wisc.edu.

[†] Department of Chemistry.

[‡] School of Pharmacy.

[§] Current address: Solid State Chemistry, Abbott, North Chicago, IL 60064.

(the β process),¹⁴ rather than the structural relaxation (the α process) of the liquid. In contrast, Tanaka views the GC mode as resulting from the extensional stress around a crystal growing in a glass because of the crystal's higher density.¹⁵ He suggests that this stress "should provide the free volume to the particles surrounding the crystal, increase their mobility, and help further crystallization." Recently, this model has been specifically formulated and applied to the systems *o*-terphenyl and salol.¹⁶

We studied the GC growth process by growing different crystal polymorphs from the same liquid to learn how crystal structure influences the phenomenon. Polymorphs are of interest here because they have different molecular packing and conformations, but grow from the same liquid; their study elucidates whether a kinetic feature of crystal growth is a property of the liquid, the crystal, or both.¹⁷ Polymorphs also enable the observation of one crystalline phase growing from another, which provides a context for crystal growth from a glass. For this study, we used the polymorphs of 5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile, named ROY for its numerous red, orange, and yellow polymorphs^{18–21} and currently the top system for the number of coexisting polymorphs of known structures (seven)²⁰ in the Cambridge Structural Database.²² We observed that some polymorphs of ROY did not show GC growth, while others did, with the latter having higher density and more isotropic molecular packing. The polymorphs not showing GC growth grew as compact spherulites at all temperatures; their growth rates near T_g decreased smoothly with falling temperature. The polymorphs showing GC growth changed growth morphologies with temperature, from faceted single crystals near the melting points, to fiber-like crystals near T_g , and to compact spherulites in the GC mode; in the GC mode, they grew at rates 10^3 – 10^4 -fold faster with activation energies 2-fold smaller than the polymorphs not showing GC growth. The GC mode had rates and activation energies similar to those of a polymorphic transformation observed near T_g . The GC mode was disrupted by the onset of the liquid's structural relaxation but could persist well above T_g (up to $1.15 T_g$) in the form of fast-growing fibers. We consider various explanations for the GC mode and suggest that it is solid-state transformation enabled by local molecular motions native to the glassy state and disrupted by the liquid's structural relaxation (the α process).

Experimental Section

ROY was obtained from Eli Lilly and Co. The growth of various polymorphs was initiated as follows: (1) spontaneous crystallization at room temperature yielded Y04 (most often), YN, and ON (least often); (2) spontaneous crystallization at room temperature following nucleation at 258 K yielded ORP in addition to the list in (1); (3) cross-nucleation between polymorphs yielded R (on Y04),²⁰ R05 (on Y04),²¹ and YN (on R) near room temperature^{20,21} and YT04 (on Y04) and R (on ORP) at 258 K; and (4) seeded crystallization yielded Y (at any temperature) and OP and YT04 (above 358 K). Seeding was performed by introducing seed crystals to liquids or by partially melting existing crystals and allowing remaining crystals to serve as seeds for subsequent experiments. The two methods of seeding had no effect on the observed crystal growth rates. Polymorphs were identified by microscopic observation (Nikon Optiphot2-Pol microscope), X-ray diffraction (Bruker D8 Advance diffractometer with Cu K_α radiation), and Raman microscopy (Renishaw System 1000 Micro-Raman spectrometer with a HeNe laser and peltier-cooled CCD detector) and through melting-point measurements (Linkam THMS 600 hot/cold stage, temperature precision ± 0.1 K).

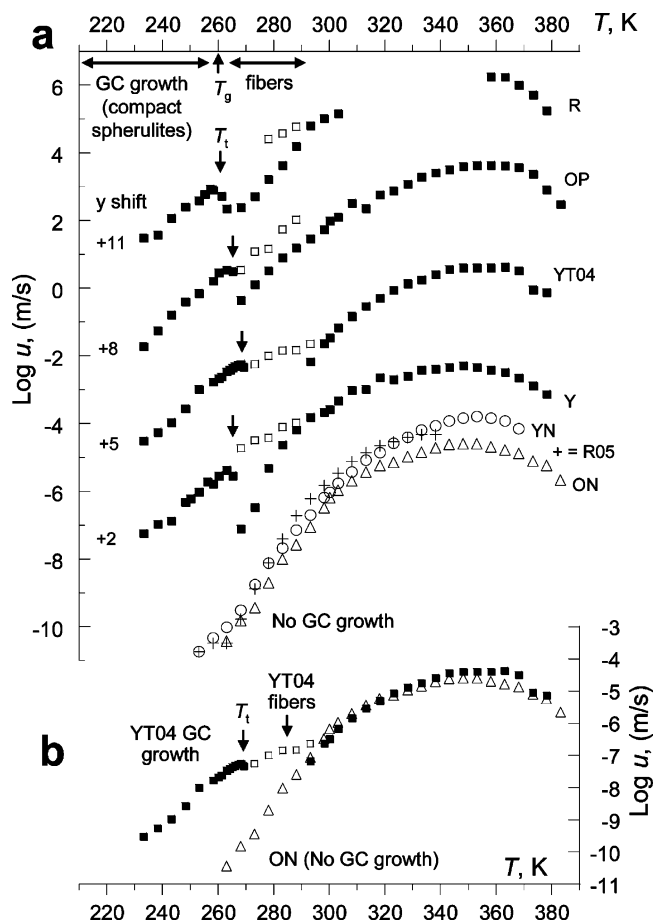


Figure 1. Growth kinetics of ROY polymorphs in offset (a) and overlay (b) views. For clarity, the overlay compares only one polymorph (YT04) that shows GC growth and another (ON) that does not. "□" are growth rates of fast-growing fibers. Data points below $\log u = -10$ are upper bounds. The growth of R05 could not be measured above 340 K because of polymorphic conversion and the fast growth of YN.

Crystal growth rates were measured with the aid of a light microscope and the Linkam hot/cold stage. ROY crystals (ca. 3 mg) were melted between two 15 mm cover glasses at 403 K for 5 min and cooled at 20 K/min to desired temperatures of crystallization. The thickness of the liquid sample was 10–15 μm and confirmed (by varying thickness from 5 to 150 μm) not to affect the growth rates. We changed the silicate cover glass to aluminum foil or Kapton (polyimide) film and observed no effect of the container material on the growth rates. The crystal growth rate was measured from the advance speed of the crystal front into the melt at a constant temperature. The time of measurement was such that the advance length of the crystal front was 0.05 mm or more. To increase experimental output, crystal growth rates were sometimes measured from growth rings developed at different temperatures.²³ For this experiment, one or more samples were placed in a DSC cell (TA Instruments Q1000), and the temperature and duration of crystallization were programmed via the DSC control. On complete crystallization, the samples were removed from the DSC cell, and the growth rings developed at different temperatures were measured through the microscope. Each crystal growth rate reported was the average of 3–6 measurements.

Results

To grow as many polymorphs as possible from the ROY liquid, we relied on spontaneous nucleation, cross-nucleation between polymorphs,^{20,21} and seeding. In all, nine polymorphs

TABLE 1: Kinetic Parameters for Crystal Growth from Liquid, Glass, or Another Crystal near T_g^a

transformation	T_i , K	$\log(u, \text{m/s})$ at T_g	$n_\alpha = u\tau_\alpha/a$ at T_g	E_a , kJ/mol	ref
ROY, $T_g = 260 \text{ K}$, $a = 7.5 \text{ \AA}$					
L \rightarrow YN	n.a.	-11.0 ^b	1	166 ± 4^c	ref 10 and this work
L \rightarrow ON	n.a.	-11.5 ^b	0.4	173 ± 6^c	
L \rightarrow R05	n.a.	-12.0 ^b	0.1	203 ± 9^c	
L/G \rightarrow YT04	269	-7.7	2700	83 ± 2	
L/G \rightarrow Y	265	-7.5	4200	76 ± 4	
L/G \rightarrow OP	265	-7.5	4200	88 ± 3	
L/G \rightarrow R	261	-8.0	1400	71 ± 4	
YN \rightarrow R	n.a.	-9.1 to -7.4	105–5300	72 ± 5	
OTP, $T_g = 243 \text{ K}$, $a = 7.7 \text{ \AA}$					
L \rightarrow C	n.a.	-12 ^b	0.1	240^c	24
L/G \rightarrow C	249	-8.1	1100	65	7
Salol, $T_g = 215 \text{ K}$, $a = 7.2 \text{ \AA}$					
L/G \rightarrow C	226	-7.7	2800	57	25
Toluene, $T_g = 117 \text{ K}$, $a = 5.9 \text{ \AA}$					
L/G \rightarrow C	116	-8.2 ^b	1100	50	26
Sulfur, $T_g = 270 \text{ K}$, $a = 6.7 \text{ \AA}$ (S_8)					
$\beta \rightarrow \alpha$	n.a.	-7.9	1900	92	27
$\gamma \rightarrow \alpha$	n.a.	-7.8	2400	92	

^a L \rightarrow X: crystalline phase X growing from liquid. L/G \rightarrow X: crystalline phase X growing from liquid and glass. Y \rightarrow X: crystalline phase X growing from crystalline phase Y. $\tau_\alpha = 100 \text{ s}$ at T_g . Error in E_a is one standard deviation. ^b Extrapolated value at T_g . ^c Kinetics are not Arrhenius. Apparent E_a was calculated at T_g . ^d Estimated from 0.7 T_m because T_g of sulfur is difficult to measure due to fast crystallization.

were grown, including the seven of known structures: R (red),¹⁸ R05 (second red form discovered in 2005),²¹ ORP (orange-red plate),¹⁸ ON (orange needle),¹⁸ OP (orange plate),¹⁸ Y (yellow),¹⁸ YN (yellow needle),¹⁸ Y04 (second yellow form discovered in 2004),²⁰ and YT04 (Y04 transformed).²⁰ The tenth known polymorph (RPL) has been observed only by depositing ROY vapor on crystals of succinic acid.¹⁹ The polymorphs could be identified on sight from their colors, morphologies, and crystal optics, but were confirmed with Raman microscopy, X-ray diffraction, and melting-point determination. The growth rates of seven polymorphs (ON, YN, R05, YT04, Y, OP, and R) could be measured near T_g (260 K) (Figure 1 and Table 1). The growth of Y04 and ORP could not be measured close enough to T_g to be of interest to this study, because other polymorphs crystallized on them (YT04 on Y04, R on ORP).

Of the seven polymorphs whose growth rates could be measured near T_g , YT04, Y, OP, and R showed GC growth, whereas ON, YN, and R05 did not. Those polymorphs showing no GC growth grew consistently as compact spherulites with sharp interfaces with the liquid at all temperatures (Figure 2), and their growth rates near T_g decreased smoothly with falling temperature. For ON and YN, X-ray analysis showed that the preferred growth direction (spherulite's radius) was the a -axis (the shortest unit cell axis), in accord with the expected anisotropy of crystal growth. For R05, this determination was impossible because its structure has not yet been solved. Below 263 K, ON, YN, and R05 grew so slowly that no significant growth could be detected before the liquid was consumed by other polymorphs that nucleated spontaneously and grew rapidly in the GC mode (mainly YT04); the data points below 263 K are upper bounds of u obtained from the longest holding times possible at each temperature (up to 48 h) and the resolution of growth measurement ($3 \mu\text{m}$). The u versus T curves of ON, YN, and R05 are approximately parallel to each other near T_g and have the bell shape that is typically observed for crystal

growth from one-component liquids. The growth kinetics of these polymorphs are not Arrhenius; the apparent activation energies E_a in Table 1 were calculated from data near T_g .

Sun et al. have described the key features of crystal growth of the ROY polymorphs showing GC growth.¹⁰ In contrast to the polymorphs not showing GC growth, these polymorphs changed growth morphologies with temperature, from faceted single crystals near the melting points, to fiber-like crystals near T_g , and to compact spherulites in the GC mode (Figure 2). The compact spherulites of the GC mode began to be observable below a well-defined temperature T_i (Table 1), which is near and slightly above T_g . They were space-filling and had sharp interfaces with the liquid. The compact spherulites of different polymorphs grew at similar rates (Figure 1 and Table 1) following Arrhenius kinetics (see Table 1 for their E_a 's). At each temperature, the growth rate of each polymorph was constant during the time of measurement (long enough to yield at least 0.05 mm of growth). At T_g , these polymorphs grew at rates 10^3 – 10^4 -fold faster with activation energies 2-fold smaller than those showing no GC growth (see Figure 1b for a comparison between YT04 and ON).

Between T_i and approximately $1.15 T_g$, fiber-like crystals were observed for the polymorphs showing GC growth. Figure 1 shows two growth rates measured in this region: the "□" (faster rates) refer to the farthest-reaching individual fibers; the "■" (slower rates) refer to the layers of fibers that thickened over time behind the individual fibers. Sun et al. showed that the compact GC growth below T_i and the fiber growth above T_i are related.¹⁰ The linear growth rates of the two morphologies fall on one smooth curve (Figure 1), showing no discontinuity at T_i . (A discontinuity does exist in the volume growth rate because the GC mode filled space and the fiber mode did not.) The relation between the two morphologies was also evident from temperature-cycling experiments. If a spherulite previously growing in the GC mode was heated to above T_i , its growth apparently stopped, but careful observations found fiber-like crystals protruding from it, growing at rates expected for the GC mode. On cooling the system again to below T_i , the GC mode resumed, but only from selected crystal/liquid interfaces. These observations led to the conclusion that the GC mode is disrupted by the liquid's structural relaxation but can still persist in the form of fast-growing fibers.

To better understand the onset and termination of the GC mode, we performed additional temperature-cycling experiments. If a spherulite of YT04 initially growing in the GC mode at 267 K (below T_i) was warmed to 270 K (above T_i) for time t_{hold} and then returned to 267 K, the resumption of GC growth depended on t_{hold} . If t_{hold} was 1 min, the growth could resume immediately at the initial growth front, with only a faint line separating the new and previous growth (Figure 3, first row). If t_{hold} was 5 min, the growth resumed at fewer sites and part of the initial growth front became inactive (Figure 3, second row). If t_{hold} was 10 min, the growth resumed at even fewer sites, yielding isolated spherulites, while the rest of the initial growth front became inactive (Figure 3, third row). As reported previously,¹⁰ if t_{hold} was 250 min, the new GC growth was initiated far away from the initial growth front, from the ends of a few, farthest-reaching fibers that had extended into the liquid.

The existence of polymorphs enabled us to study the growth of a crystalline phase not only from the liquid and glass but also from another crystalline phase. The conversion of polymorph YN to R was readily observed near T_g . This conversion was initiated by holding a sample of YN at 313 K. Isolated red

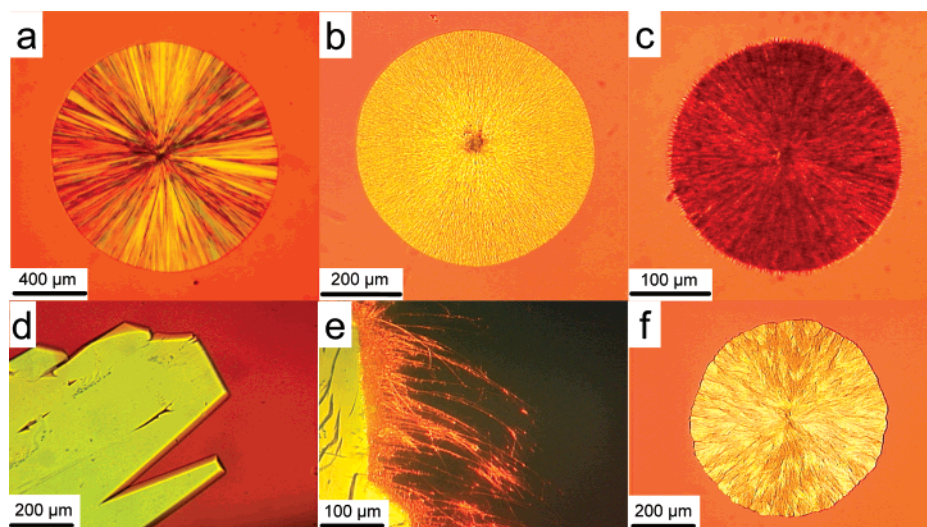


Figure 2. Growth morphologies of ROY polymorphs. ON (a), YN (b), and R05 (c) grew consistently as spherulites; their growth slowed smoothly with falling temperature (Figure 1), showing no GC mode. YT04, Y, OP, and R showed GC growth, and their morphologies changed with temperature. This morphological change is illustrated in (d), (e), and (f) using YT04. (d) Faceted single-crystal growing near the melting point T_m . (e) Fibers growing between T_i and ca. $1.15 T_g$ from a single crystal previously formed near T_m . (f) A spherulite growing below T_i in the GC mode. The pictures were taken with plane-polarized light, except for (e) for which crossed polarizers were used to reveal the fibers.

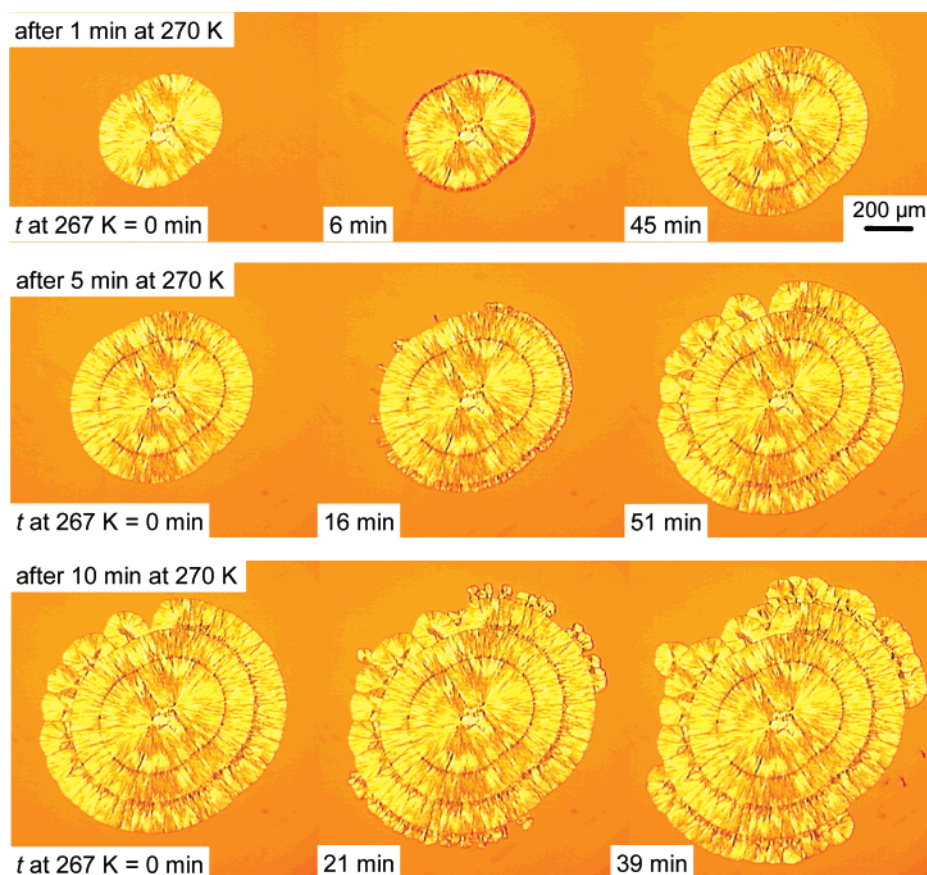


Figure 3. Temperature-cycling experiments performed with YT04 crystals grown at 267 K in the GC mode. The sample was heated to 270 K (above $T_i = 269$ K) for 1, 5, and 10 min and returned to 267 K to observe the resumption of GC growth.

single crystals of R appeared over time, consuming the yellow crystals that comprised the spherulites of YN. Figure 4 compares the morphologies of R grown from the amorphous phase (a) and from polymorph YN (b). The growth from YN yielded faceted crystals with uniform extinction between crossed polarizers and color changes in plane-polarized light. The growth of R from the amorphous phase, in contrast, yielded polycrystalline spherulites of fine texture, which were nearly opaque.

As compared to faceted crystals grown from a liquid near the melting point, the R crystals grown from YN had rougher surfaces and lines in parallel with crystal edges. The rate of YN-to-R conversion from $T_g - 12$ K to $T_g + 38$ K was measured (Figure 4c). The conversion rates varied depending upon the direction in which the faceted-growth was measured (e.g., 1 or 2 in Figure 4b) and the orientation with which an R crystal was nucleated relative to the cover glasses confining

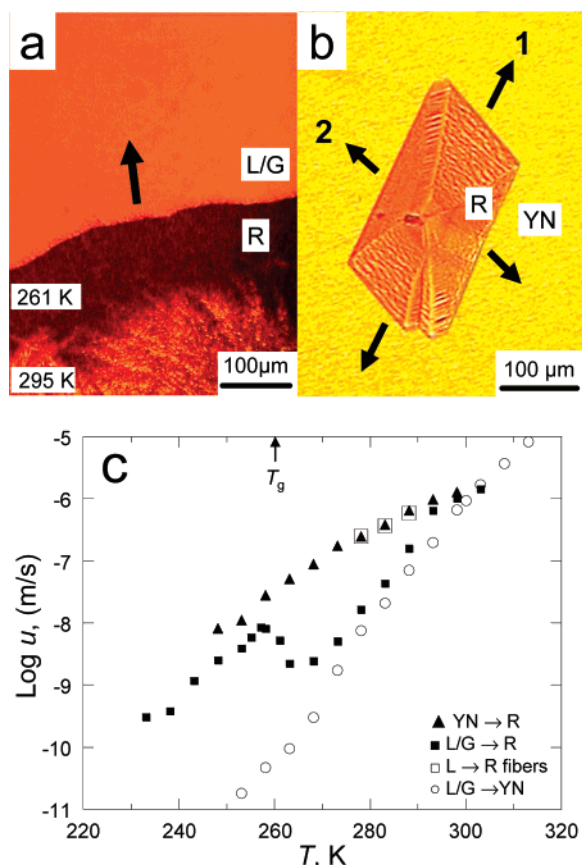


Figure 4. Morphologies of polymorph R growing at 261 K from (a) liquid/glass (L/G) and (b) polymorph YN. (c) Comparison of growth rates of R from YN and of R and YN from the amorphous phase (L/G). Data points below $\text{Log } u = -10$ are upper bounds. The fastest set of growth rates of R from YN is shown; the other data sets are offset from this set by less than 1.7 decades.

the liquid, but had the same temperature dependence. Shown in Figure 4c is the fastest set of growth rates; the other data sets are offset from this set of data by less than 1.7 decades. The growth kinetics were Arrhenius, and the activation energy E_a was 72 ± 5 kJ/mol, which is similar to that for the GC growth of R (71 ± 4 kJ/mol). As expected for a solid–solid process, no discontinuity occurred in the YN-to-R conversion rate at T_g . The growth of R from YN (a solid) was often observed to be faster than the growth of R from the liquid above T_g .

Discussion

Which Crystal Properties Correlate with the Existence of the GC Mode? Whether or not a ROY polymorph exhibits GC growth has no correlation with its thermodynamic stability; for example, the GC polymorph R has stability intermediate between two polymorphs showing no GC growth, ON (more stable than R) and YN (less stable than R). The polymorphs' relative stability was obtained from their interconversions and by extrapolating their free energy versus temperature curves determined at higher temperatures.²¹ The existence of the GC mode also has no correlation with the polymorph's molecular conformation: YT04, Y, and YN have nearly the same molecular conformation (i.e., twist angle across the central C–N bond), which differs substantially from those in the other polymorphs, and yet the three polymorphs fall in different groups.

A correlation does exist between the existence of the GC mode and the polymorph's density. Polymorphs showing GC growth are denser than those not showing this growth mode: d

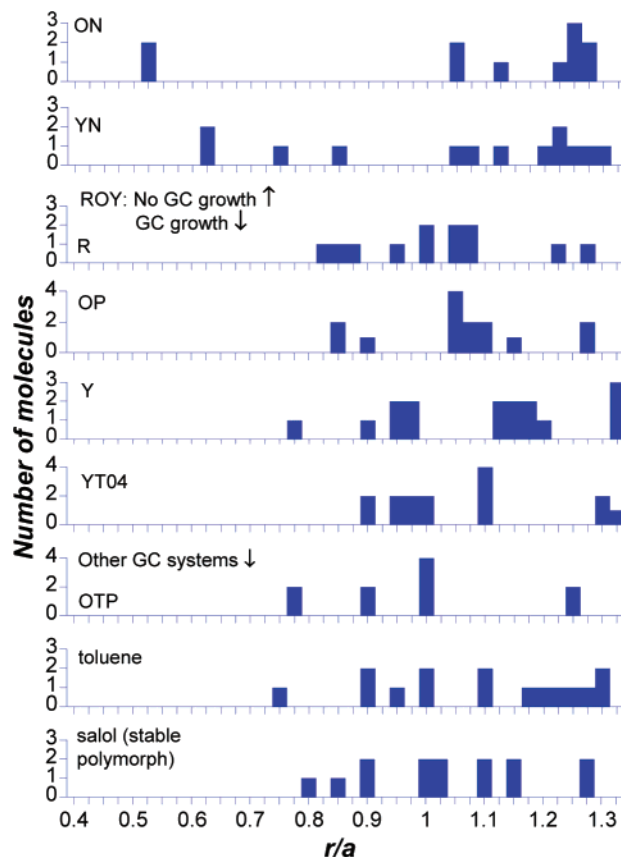


Figure 5. Radial distribution functions of molecular centers of mass in ROY polymorphs scaled by a (molecular diameter). Data are also shown for other crystals capable of GC growth. The a values used were: 7.5 Å for ROY, 7.7 Å for *o*-terphenyl, 7.2 Å for salol, and 5.9 Å for toluene.

(g/cm^3) = 1.473 (YT04), 1.447 (Y), 1.438 (R), 1.435 (OP), 1.431 (YN), and 1.428 (ON) (all values at 298 K).^{18,20} YT04, the densest polymorph, has the highest onset temperature T_i for GC growth, although the T_i 's for the other GC polymorphs do not follow their density order precisely (Table 1). The GC growth rates at the same temperature have no correlation with the polymorphs' densities. These observations suggest a possible connection between the crystal density and the existence of the GC mode, but it is unclear which properties of GC growth are predictable from the crystal density.

A correlation also exists between the existence of the GC mode and the anisotropy of molecular packing. Figure 5 shows the radial distribution function (RDF) of molecular centers of mass in each crystal polymorph. To compare different molecules, we normalized distance by the molecular diameter a . For this calculation, we treat molecules as spheres packing closely to occupy 74% of space and solve for the diameter of the sphere a that gives the density of the crystal; $a = 1.12V^{1/3}$, where V is the unit cell volume per molecule. In polymorphs YN and ON (no GC growth), the distribution of neighboring molecules around a central molecule is highly anisotropic, with some neighbors close by and others far away. In polymorphs showing GC growth, the distribution of neighboring molecules is closer to being equally distant from a central molecule. Because a liquid is expected to have an isotropic distribution of molecules, the structures of the polymorphs showing GC growth are expected to be more liquid-like than those showing no GC growth. It is possible that this similarity of structure allows the GC process to occur with little center-of-mass reorganization, as discussed below. As shown in Figure 5, other

molecules that show GC growth also have isotropic local packing in the crystal. For the case of OTP, a liquid-state RDF is available from computer simulations.²⁸ It agrees reasonably well with the RDF of the OTP crystal, supporting the view that crystals showing GC growth have liquid-like packing.

Relationship between the GC Growth Mode and Structural Relaxation in the Liquid. Crystal growth requires movement of molecules. For crystal growth from a liquid, a strong correlation exists between the growth kinetics and the structural relaxation (or diffusion) of the bulk liquid; this is the basis of the Wilson–Frenkel approach^{1,2} for describing crystal growth from the melt. It is of interest to determine whether the same relation exists for the GC growth. For this purpose, we calculate the number of molecular layers that are added to the crystalline phase in one structural relaxation time τ_α at T_g : $n_\alpha = u\tau_\alpha/a$, where a is the molecular diameter and $\tau_\alpha \approx 100$ s at T_g . For diffusion-controlled crystal growth in many one-component liquids, $n_\alpha < 1$ holds,⁵ indicating substantial α relaxation or diffusion is possible during the time for one molecular layer to be added to the crystalline phase. We find $n_\alpha = 0.1$ – 1 for the growth of the polymorphs not showing the GC mode. In contrast, we find $n_\alpha = 1700$ – 4200 for the GC growth of ROY, and similar values for other GC systems (Table 1). These values indicate that for crystals growing in the GC mode, no substantial α relaxation or diffusion is possible during the time required for one molecular layer to be added to the crystalline phase.

The fast crystal growth in the GC mode can also be appreciated in reference to the time scale of molecular rotation τ_{rot} , recalling that $\tau_\alpha \approx \tau_{\text{rot}}$ for a typical molecular liquid without significant internal flexibility.²⁹ Complex organic molecules like ROY must reorient, at least partially, to crystallize. The growth rates of the polymorphs showing no GC growth are such that during the time for adding one layer of molecules to the crystalline phase, the molecules in the liquid can undergo substantial reorientation. In contrast, the growth rates of the polymorphs showing GC growth are so fast that molecules have little time to rotate (typically $10^{-3} \tau_{\text{rot}}$) before being incorporated into the crystalline phase. The comparisons above indicate that the bulk structural relaxation time of the liquid is too slow to be the kinetic process that explains fast GC growth.

The view that GC growth rates are not controlled by structural relaxation in the bulk liquid is supported by the similarity between the kinetics of the GC growth and the YN-to-R polymorphic transformation (Figures 1 and 4 and Table 1). This similarity argues that GC growth could be viewed as a solid-state transformation. Despite extremely slow molecular diffusion and rotation in a solid, solid-state transformations manage to occur rapidly: the growth of polymorph R can be faster from polymorph YN than from the liquid at the same temperature; the transformation between sulfur polymorphs is facile even near its T_g ;²⁷ the growth of one crystal grain into another is readily observed in polycrystalline solids well below the melting point.^{30,31} The low bulk molecular mobility in crystals suggests that solid-state transformations are made possible by molecular motions at the interface. Interfacial diffusion can be substantially faster than bulk diffusion; for example, self-diffusion in polycrystalline naphthalene³² is orders of magnitude faster than that in single-crystal naphthalene.³³ Thus, one explanation of why GC growth can be much faster than diffusion-controlled growth is that a solid-state transformation need not utilize “bulk-like” motions.

Models for GC Growth

We now evaluate three models for GC growth, including two from the literature (homogeneous nucleation-based (HNB) crystallization⁷ and tension-induced interfacial mobility^{15,16}) and a third proposed here (solid-state crystal growth by local mobility). These models make different assumptions about which molecular motions are responsible for GC growth and whether homogeneous nucleation is a key step of GC growth. The HNB model assumes that GC growth occurs via the coalescence of homogeneous crystal nuclei onto existing crystal surfaces at a rate defined by the β relaxation of the liquid, rather than the α relaxation.^{7,8} The model of tension-induced interfacial mobility^{15,16} postulates that GC growth is the same as crystal growth in the diffusion-controlled mode, except that diffusion is enhanced at the crystal/liquid interface due to the tension created by the density difference between the crystal and the liquid. Because a crystal usually is denser than a liquid or a glass, crystal growth may induce extensional stress around a crystal due to volume contraction. While some argue that this stress should slow crystal growth (e.g., by thermodynamically destabilizing the crystal³⁴), Tanaka suggests that this stress “should provide the free volume to the particles surrounding the crystal, increase their mobility, and help further crystallization.” This process would be possible only at temperatures so low that flow cannot relieve the stress on the time scale of crystal growth.

The model of solid-state crystal growth by local mobility assumes that the molecular motions responsible for GC growth are not the α process (the motion responsible for diffusion-controlled growth), but a local molecular motion native to the glassy (solid) state. An example of local molecular motions in the glass is the β process. In making this assumption, this model is similar to the HNB model, but it does not invoke homogeneous nucleation as a key step of GC growth. It assumes that certain crystal structures can grow by local molecular fluctuations because their formation requires relatively minor molecular rearrangement of the liquid’s structure. This model makes an analogy between crystal growth in the glass and crystal growth in other solids (e.g., from another polymorph). In this model, GC growth is a new mode of growth (distinct from diffusion-controlled growth) for which the α relaxation is not only unnecessary but also detrimental.

We evaluate these three models against known features of GC growth, including its kinetics, its dependence on temperature and temperature cycling, and its dependence on polymorph. To recap, GC growth is characterized by a higher growth rate u and a smaller activation energy E_a than diffusion-controlled growth, a time-independent u , and similar kinetics as a polymorphic transformation (YN-to-R). The dependence of the GC mode on temperature and temperature cycling refers to its abrupt onset and termination near T_g , its persistence up to ca. $1.2 T_g$ as fast-growing fibers, and its selective resumption after temperature cycling across its onset temperature T_i . The polymorphic dependence of the GC mode refers to its correlation with the polymorph’s density and molecular packing. In our view, none of these three explanations satisfactorily accounts for all of the features, but the model of solid-state crystal growth by local mobility comes the closest.

Homogeneous-Nucleation-Based (HNB) Crystallization.

To calculate the rate of GC growth, this model uses the rate of homogeneous nucleation, the size of critical nuclei, and the frequency of the β relaxation. It is difficult to assess whether this procedure generally predicts higher u and lower E_a for GC growth than for diffusion-controlled growth, in part because

several model parameters are not known with confidence (crystal/liquid interfacial energy and distance from the crystal surface at which nucleation occurs). The emphasis of this model on homogeneous nucleation seems unusual because the GC mode is apparently a phenomenon of crystal growth. This model makes no specific predictions about the time dependence of u and the correlation of GC growth with crystal density and packing. It has difficulty explaining the effect of temperature and temperature cycling on GC growth. For example, it would require a change of nucleation rate by orders of magnitude with a small temperature change (a few degrees) to explain the abrupt onset and termination of GC growth; it would require a spatially heterogeneous reactivation of homogeneous nucleation to explain the resumption of GC growth at some but not all crystal/liquid interfaces upon temperature cycling.

Tension-Induced Interfacial Mobility. This model can explain why GC growth has a larger u and smaller E_a than diffusion-controlled growth. It obtains the rate of GC growth from the rate of diffusion-controlled growth with an adjustment for free volume that is created and trapped at the crystal/liquid interface as a result of crystal growth in a slow-flowing liquid.¹⁶ This model would explain the abrupt onset (termination) of GC growth by the abrupt increase (decrease) of free volume at the crystal/liquid interface as the liquid loses (gains) ability to flow. It could explain why the GC mode can resume after brief exposure to high temperature, but cannot resume after longer exposures: short exposure to high temperature does not allow sufficient time to relax the stress that allows GC growth, while longer exposure to high temperature destroys both the tension and the growth. In its present form, the model provides no explanation for the selective resumption of GC growth after temperature cycling.

This model can explain why the polymorphs that show GC growth are denser than those that do not: the growth of a denser polymorph should lead to greater volume contraction, higher tension at the crystal/liquid interface, and higher interfacial molecular mobility. The transition temperature T_i would be expected to be ordered by density according to this model; with one exception (OP), this expectation is fulfilled. For this model, one might imagine that GC growth rates would also correlate with the crystal–liquid density difference. Konishi and Tanaka used the density difference of 1.1% between two salol polymorphs to explain their growth rate difference of approximately 10-fold.¹⁶ A similar effect, however, is not observed for ROY polymorphs: the polymorphs showing GC growth differ in density by as much as 2.5% but have similar growth rates. This model would have nothing to say about the differences in packing between the polymorphs that do and do not show GC growth (Figure 5) except to attribute it as a secondary effect slaved to some relationship between packing and density.

This model has difficulty explaining the time-independent u : because the tension at the crystal/liquid interface builds with the progress of crystal growth, it would predict that u increases with time. It is also difficult for it to explain the kinetic similarity of GC growth with polymorphic conversion because the latter can occur with much smaller density changes than GC growth and even with negative density changes.³⁵ This model seems inconsistent with the fast fiber growth associated with the GC mode that persists up to $1.2 T_g$; stress should be rapidly dissipated at these temperatures particularly for a one-dimensional object like a fiber.

Solid-State Crystal Growth by Local Mobility. This model also can explain why GC growth has faster u and lower E_a than diffusion-controlled growth. It assigns the fast-growing fibers

in the equilibrium liquid as precursors of GC growth¹⁰ and obtains their growth rate near and below T_g from the temperature dependence of an appropriate local molecular motion responsible for GC growth. This procedure yields faster u and lower E_a for GC growth because local motions have higher frequencies and weaker temperature dependence than the α process. Because fast-growing fibers appear at a temperature ($1.2 T_g$) typical for the bifurcation of the α and β processes, it would be reasonable to associate GC growth with the β process. This view would predict the ratio of the growth rates for the GC mode and the diffusion-controlled mode to be $u_{GC}/u_{DC} \approx \tau_\alpha/\tau_\beta$. For *o*-terphenyl, the estimate is $u_{GC}/u_{DC} \approx 10^6$ at T_g .³⁶ The ratio just obtained should be reduced to account for the inexact tracking of u_{DC} and τ_α , a result of the decoupling of diffusion and viscous flow.⁴ For *o*-terphenyl, the corrected prediction for u_{GC}/u_{DC} is 10^4 , in approximate agreement with experiment.

This model assumes that crystal structures capable of GC growth are those sufficiently similar to the structure of the glass (or liquid) such that minor structural rearrangements suffice to transform the amorphous state into a crystal. It can therefore explain why the polymorphs that show GC growth are all more isotropically packed than those that do not. This expectation is based on the assumption that the liquid/glass structure of ROY has isotropic packing. For ROY, we can justify this statement only based upon the greater similarity of the X-ray diffraction pattern of the liquid with the polymorphs showing GC growth than with the polymorphs not showing GC growth. For OTP, simulations²⁸ suggest similar packing between the structures of the liquid and the crystal (which shows GC growth), supporting the basis for this explanation of GC growth. There is no strong argument that center-of-mass RDF is the best measure of structural similarity between the crystalline and amorphous states. If detailed information about the relative orientation of neighboring molecules in the liquid were available, perhaps from a simulation, it would be interesting to compare this measure of structural similarity against the polymorphs that do and do not show GC growth. This model has nothing to say about the correlation of the GC mode with the density of the polymorph, except to argue that this is a secondary effect slaved to some relationship between packing and density.

The possibility that different polymorphs can grow at substantially different rates and activation energies is supported by the simulation of crystal growth in a Lennard-Jones liquid, wherein the fcc (100) face grows “diffusionless” and without activation barrier,³⁷ while the fcc (111) face grows diffusion-controlled and thermally activated.³⁸ These simulations also confirm that the structure of the liquid at the interface with the crystal can play a critical role in determining whether or not diffusionless growth is observed.

This model does not make a specific prediction for the time dependence of u . Whether tension exists at the phase boundary during GC growth remains an unresolved question. Given the ambiguity, one can envision two scenarios simultaneously compatible with this model and time-independent u : (1) local molecular motions do not depend strongly on tension at the interface; (2) little tension exists at the interface. GC growth yields a polycrystalline material with small grains and residual entropy at 0 K;⁷ it is possible that voids exist between grains, leading to a polycrystalline material of comparable overall density as the glass and little tension at its interface with the glass.

This model would attribute the disruption of the GC mode by heating to structural changes at the crystal/amorphous interface caused by the liquid’s structural relaxation. The fact

that prolonged exposure to higher temperature can suppress GC growth (Figure 3) argues that the interfacial structure maintained during GC growth differs from the relaxed interfacial structure. For GC growth to propagate at a steady rate, that interfacial structure must be maintained. If the exposure to high temperature is short (Figure 3, first row), there is insufficient time for structural relaxation at the crystal/liquid interface, and when the temperature is lowered, fast growth can resume. Longer exposures to high temperature, however, allow structural relaxation at the interface, thus destroying the structural similarity that allows fast crystal growth (Figure 3, second and third rows). This model would explain the persistence of GC growth well above T_g in the form of fast-growing fibers by the persistence of local molecular motions characteristic of the glassy state in the equilibrium liquid. Alternately, one could invoke the known spatial heterogeneity in the dynamics of deeply supercooled liquids.³⁹ If some regions of the liquid in contact with the GC interface are relaxing slowly, fast crystal growth is possible at least in some directions. To explain the selective resumption of GC growth at the ends of the farthest-reaching fibers,¹⁰ this model would argue that the farthest-reaching fibers were actively growing and their growth fronts have the required interfacial structure for GC growth. When the temperature is lowered, they become the sites at which GC growth resumes.

One difficulty this model faces is explaining why despite the different local packing in YN and R polymorphs, the YN-to-R transformation is fast. It is possible that the analogy between GC growth and polymorphic conversion is apt only to the extent that both occur by local, not large-scale, molecular motions. Polymorph R grows as faceted single crystals from polymorph YN but as polycrystalline spherulites from the glass. This argues that the details of local molecular motions responsible for crystal growth differ for the order–order and disorder–order transformations. It could be this difference that allows the growth of many polymorphs from the glass at comparable rates but the preferential growth of R from YN, even though the growth of other polymorphs is thermodynamically allowed.

Conclusions

We studied the onset of the fast, diffusionless crystal growth near T_g (the GC mode) by growing seven polymorphs from the liquid of ROY, currently the top system for the number of coexisting polymorphs of known structures. Some polymorphs did not show GC growth, while others did, with the latter having higher density and more isotropic molecular packing. The polymorphs not showing GC growth grew as compact spherulites at all temperatures; their growth rates near T_g decreased smoothly with falling temperature. The polymorphs showing GC growth changed growth morphologies with temperature, from faceted single crystals near the melting points, to fiber-like crystals near T_g , and to compact spherulites in the GC mode; in the GC mode, these polymorphs grew at rates 3–4 orders of magnitude faster and activation energies 2-fold smaller than the polymorphs not showing GC growth. The GC mode had rates and activation energies similar to those of a polymorphic transformation observed near T_g . The GC mode was disrupted by the onset of the liquid's structural relaxation but could persist well above T_g (up to 1.15 T_g) in the form of fast-growing fibers. We evaluated three models for GC growth against its known features: homogeneous nucleation-based crystallization, tension-induced interfacial mobility, and solid-state crystal growth by local mobility. We find merits and flaws in each model, but favor the view that GC growth is solid-state crystal growth

achieved by local molecular motions native to the glassy state and disrupted by the liquid's structural relaxation (the α process). Better understanding of the phenomenon may benefit from studying additional polymorphic systems in which high density does not correlate with isotropic packing such that opposing models can be better tested, altering crystal–liquid density difference by pressure, and characterizing the nature of the polycrystalline material produced by GC growth.

Acknowledgment. We thank the University of Wisconsin – Madison, the Donors of the American Chemical Society Petroleum Research Fund, the NSF-funded UW MRSEC, and NSF Chemistry (0605136) for supporting this work. We thank Peter Harrowell for discussions.

References and Notes

- (1) Wilson, H. A. *Philos. Mag.* **1900**, 50, 238–251.
- (2) Frenkel, J. *Phys. Z. Sowjet Union* **1932**, 1, 498–500.
- (3) Ngai, K. L.; Magill, J. H.; Plazek, D. J. *J. Chem. Phys.* **2000**, 112, 1887–1892.
- (4) Mapes, M. K.; Swallen, S. F.; Ediger, M. D. *J. Phys. Chem. B* **2006**, 110, 507–511.
- (5) Ediger, M. D.; Harrowell, P.; Yu, L. *J. Chem. Phys.* **2008**, 128, 034709/1–034709/6.
- (6) Greet, R. J.; Turnbull, D. *J. Chem. Phys.* **1967**, 46, 1243–1251.
- (7) Hikima, T.; Adachi, Y.; Hanaya, M.; Oguni, M. *Phys. Rev. B* **1995**, 52, 3900.
- (8) Hatase, M.; Hanaya, M.; Oguni, M. *J. Non-Cryst. Solids* **2004**, 333, 129–136.
- (9) Ishida, H.; Wu, T.; Yu, L. *J. Pharm. Sci.* **2007**, 96, 1131–8.
- (10) Sun, Y.; Xi, H.; Ediger, M. D.; Yu, L. *J. Phys. Chem. B* **2008**, 112, 661–664.
- (11) Uhlmann, D. R.; Uhlmann, E. V. In *Nucleation and Crystallization in Liquids and Glasses*; Weinberg, M. C., Ed.; The American Ceramic Society: Westerville, OH, 1993.
- (12) Spinella, C.; Lombardo, S.; Priolo, F. *J. Appl. Phys.* **1998**, 84, 5383–5414.
- (13) Koster, U.; Meinhardt, J. *Mater. Sci. Eng.* **1994**, A178, 271–278.
- (14) Hikima, T.; Hanaya, M.; Oguni, M. *J. Non-Cryst. Solids* **1998**, 235–237, 539–547.
- (15) Tanaka, H. *Phys. Rev. E* **2003**, 68, 011505-1–011505-8.
- (16) Konishi, T.; Tanaka, H. *Phys. Rev. B* **2007**, 76, 220201-1–220201-4.
- (17) Wu, T.; Yu, L. *J. Phys. Chem. B* **2006**, 110, 15694–15699.
- (18) Yu, L.; Stephenson, G. A.; Mitchell, C. A.; Bunnell, C. A.; Snorek, S. V.; Bowyer, J.; Borchardt, T. B.; Stowell, J. G.; Byrn, S. R. *J. Am. Chem. Soc.* **2000**, 122, 585.
- (19) Mitchell, C. A.; Yu, L.; Ward, M. D. *J. Am. Chem. Soc.* **2001**, 123, 10830.
- (20) Chen, S.; Guzei, I. A.; Yu, L. *J. Am. Chem. Soc.* **2005**, 127, 9881.
- (21) Chen, S.; Xi, H.; Yu, L. *J. Am. Chem. Soc.* **2005**, 127, 17439.
- (22) Allen, F. H. *Acta Crystallogr.* **2002**, B58, 380.
- (23) Yu, L. *Cryst. Growth Des.* **2003**, 3, 967–971.
- (24) Magill, J. H.; Li, H. M. *J. Cryst. Growth* **1973**, 20, 135–44.
- (25) Hanaya, M.; Hikima, T.; Hatase, M.; Oguni, M. *J. Chem. Thermodyn.* **2002**, 34, 1173.
- (26) Hatase, M.; Hanaya, M.; Hikima, T.; Oguni, M. *J. Non-Cryst. Solids* **2002**, 307–310, 257–263.
- (27) Briske, C.; Hartshorne, N. H. *Trans. Faraday Soc.* **1967**, 63, 1546–52.
- (28) Mossa, S.; Di Leonardo, R.; Ruocco, G.; Sampoli, M. *Phys. Rev. E* **2000**, 62, 612–630.
- (29) Ediger, M. D.; Angell, C. A.; Nagel, S. R. *J. Phys. Chem.* **1996**, 100, 13200–13212.
- (30) McCrone, W. C.; Cheng, P. T. *J. Appl. Phys.* **1949**, 20, 230–231.
- (31) Nam, T. N.; Otoh, S.; Masuda, T. *Tectonophysics* **1999**, 304, 57–70.
- (32) Sherwood, J. N.; White, D. J. *Philos. Mag.* **1967**, 16, 975–80.
- (33) Sherwood, J. N.; White, D. J. *Philos. Mag.* **1967**, 15, 745–53.
- (34) Schmelzer, J. W. P.; Zanotto, E. D.; Avramov, I.; Fokin, V. M. *J. Non-Cryst. Solids* **2006**, 352, 434–443.
- (35) Bradley, R. S. *J. Phys. Chem.* **1956**, 60, 1347–1354.
- (36) Wagner, H.; Richert, R. *J. Phys. Chem. B* **1999**, 103, 4071–4077.
- (37) Broughton, J. Q.; Gilmer, G. H.; Jackson, K. A. *Phys. Rev. Lett.* **1982**, 49, 1496–500.
- (38) Burke, E.; Broughton, J. Q.; Gilmer, G. H. *J. Chem. Phys.* **1988**, 89, 1030–41.
- (39) Ediger, M. D. *Annu. Rev. Phys. Chem.* **2000**, 51, 99.