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Fast Crystal Growth from Organic Glasses: Comparison of o-Terphenyl with its Structural Analogs

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Ⓢ *Supporting Information*

ABSTRACT: Crystal growth kinetics and liquid dynamics of 1,2-diphenylcyclopentene (DPCP) and 1,2-diphenylcyclohexene (DPCH) were characterized by optical microscopy and dielectric spectroscopy. These two molecules are structurally homologous and dynamically similar to the well-studied glassformer *ortho*-terphenyl (OTP). In the supercooled liquid states of DPCP and DPCH, the kinetic component of crystal growth u_{kin} has a power law relationship with the primary structural relaxation time τ_α, $u_{kin} \propto \tau_\alpha^{-\xi}$ ($\xi \approx 0.7$), similar to OTP and other fragile liquids. Near the glass transition temperature (T_g), both DPCP and DPCH develop much faster crystal growth via the so-called GC (glass to crystal) mode, again similar to the behavior of OTP. We find that the α-relaxation process apparently controls the onset of GC growth, with GC growth possible only at sufficiently low fluidity. These results support the view that GC crystal growth can only occur in systems where the liquid and crystal exhibit similar local packing arrangements.
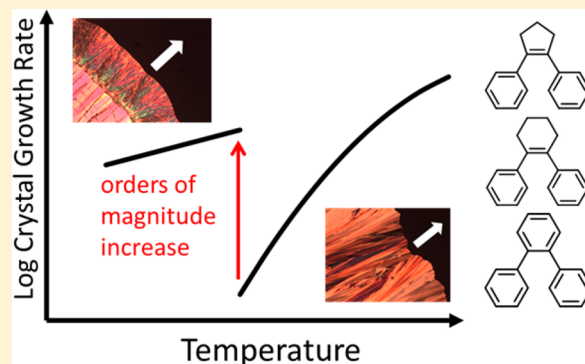
■ INTRODUCTION

Glasses represent hybrid materials that combine the local disorder of the liquid state with the mechanical rigidity of the crystalline state.[1−3] In common with the liquid state, glasses can be extremely homogeneous on macroscopic length scales and glass mixtures of many different compositions can be formed. However, glasses are generally thermodynamically unstable with respect to crystallization, and this can severely limit potential applications. As examples, consider the molecular glasses that are of increasing importance in the fields of pharmaceutics[4−6] and organic electronics.[7,8] The advantages of the glassy state include higher dissolution rates and bioavailability for pharmaceutics and structures for electronic components that are free of grain boundaries and other defects. In order to maintain these advantages crystallization must be avoided. As such, a fundamental understanding of the processes by which molecular glasses crystallize is important.

Crystal growth rates for single component organic liquids are reasonably well understood for a broad temperature range above the glass transition temperature (T_g).[9−11] Just below the melting point, the rate of crystallization is limited by the thermodynamic driving force. As the temperature is lowered, the thermodynamic driving force increases and the crystal growth rate increases. Further supercooling eventually brings about a reduction in growth rate as growth becomes limited by molecular diffusion, which is slowing dramatically as T_g is approached.[12]

In addition to these two crystal growth regimes, some molecular liquids and glasses exhibit unusually rapid crystal growth that occurs near and below T_g, the so-called glass-to-crystal (GC) mode. The transition into the GC mode is marked by a sharp *increase* in growth rate with *decreasing* temperature. This occurs at a transition temperature T_t, the highest temperature at which the GC mode is fully active. GC crystal growth is several orders of magnitude faster than the extrapolated growth rates from the diffusion-controlled regime in the supercooled liquid. GC crystal growth has been observed for about 12 organic glassformers but has not yet been observed for other classes of materials. Several theories have been proposed to explain this very fast crystal growth from the glass: homogeneous-nucleation based crystallization,[13] tension-induced mobility,[14] solid-state transformation by local mobility,[15] percolative nanocrystallization,[16] and shear-stress-induced mobility without negative pressure.[17] At this time no model is complete in predicting all aspects of GC growth. This lack of understanding limits our ability to predict the long-term stability of organic glasses.

In this study we examine the crystal growth properties and liquid dynamics of 1,2-diphenylcyclopentene (DPCP) and 1,2-

diphenylcyclohexene (DPCH). These cyclic stilbenes were introduced by Ping et al. as structural analogues of the well-studied molecular glassformer o-terphenyl (OTP).[18] In DPCP and DPCH, the central aromatic ring of OTP is replaced by a partially aliphatic ring containing 5 and 6 carbons, respectively (see Figure 1 below). Ping et al. determined the critical cooling rates for glass formation for these molecular liquids and two other cyclic stilbenes, in an effort to understand why OTP is such a good glassformer. Here we extend the comparison of OTP and cyclic stilbenes to include the measurement of crystal growth rates and liquid dynamics over a wide range of temperatures.

Measurements of the dynamics of liquids and glasses of DPCP and DPCH were carried out via dielectric spectroscopy. These measurements allow for the crystal growth rates to be examined in the context of molecular motions native to the liquid and glassy states. We report that in the diffusion-controlled regime, DPCP and DPCH both exhibit a power law relationship between the crystal growth rate u and the structural relaxation time τ_α: $u \propto \tau_\alpha^{-\xi}$ ($\xi \approx 0.7$). This relationship is consistent with the behavior of OTP and other fragile liquids.[19]

OTP is known to display GC growth,[20,21] and we show here that DPCP and DPCH also develop the GC growth mode. In addition to their structural similarity, we show that liquids of these three molecules have structural relaxation times τ_α with very similar temperature dependences. These three structurally and dynamically similar molecules allow a careful investigation into the factors that influence GC growth. The results make a strong argument for the importance of τ_α in determining the condition under which GC growth is activated and argue against a role for the observed β-relaxation processes as the kinetic origin for the GC process.

We also consider the role of the crystal structure in determining whether or not a particular system will show GC crystal growth. In a study of ROY (5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile), the crystal growth of seven polymorphs into the same liquid was examined.[15] Only those polymorphs with liquid-like packing were found to exhibit GC growth. Here we report that the crystal packing of DPCP and DPCH is similar to that of OTP and consistent with other crystal structures known to exhibit GC growth.

■ MATERIALS AND METHODS

The syntheses of 1,2-diphenylcyclopentene (DPCP) and 1,2-diphenylcyclohexene (DPCH) are described in detail elsewhere.[18] Samples for dielectric spectroscopy were prepared by melting either DPCP or DPCH between 30 mm and 20 mm diameter electrodes with a 25 μm thick Teflon ring used as a spacer (14 mm i.d. and 20 mm o.d.). The resulting capacitor was placed in a sample holder and reheated to above the sample melting temperature. The sample holder was then cooled via a precooled nitrogen-gas filled cryostat with a Novocontrol Quatro temperature controller. This procedure resulted in initial cooling rates in excess of 50 K/min slowing as the sample thermally equilibrated. The α-process was measured using a Solartron SI-1260 gain-phase analyzer equipped with a Mestec DM-1360 transimpedance amplifier. The β and γ processes were measured using an ultrahigh precision capacitance bridge (Andeen-Hagerling AH-2700A). The shapes of the dielectric loss spectra for the α-processes were characterized in reference to the Kohlrausch−Williams−Watts equation, $\exp[-(t/\tau)^\beta]$, as described below.

Crystal growth rates of DPCP and DPCH were determined by polarized light optical microscopy (Olympus BX53) with temperature controlled via a liquid nitrogen cooled hot/cold stage (Linkam THMSE 600) with temperature stability of ± 0.1 K. Samples for measurement were prepared by melting ~3 mg of material at T_m + 5 K for 3 min between 15 mm diameter circular coverslips resulting in an ~10 μm thick sample. Crystal growth was initiated by spontaneous nucleation or crystal seeding as needed. Only one crystal structure is known for DPCP and DPCH; this was confirmed with Raman spectroscopy (Thermo Scientific DXR Raman Microscope, λ = 532 nm).

■ RESULTS

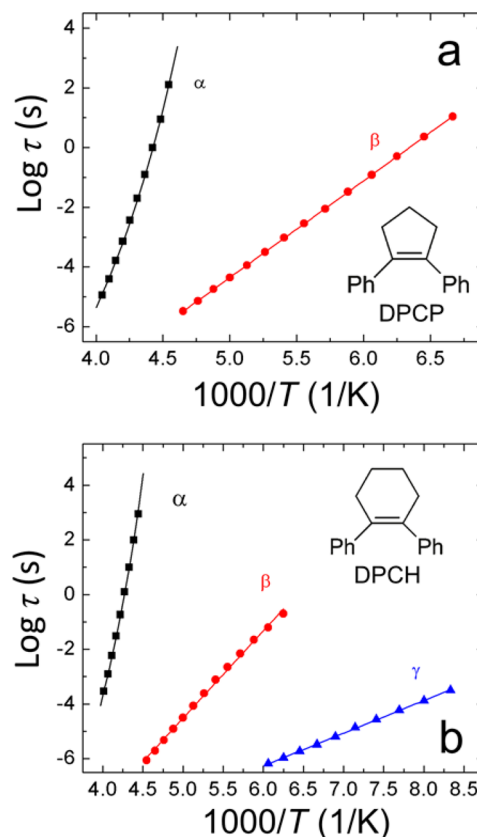**Dielectric Relaxation.** The dielectric relaxation times for DPCP are shown in Figure 1a. The measurement range for the

Figure 1. Dielectric relaxation times for the primary α-relaxation and the β-relaxation of 1,2-diphenylcyclopentene (DPCP) (a) and 1,2-diphenylcyclohexene (DPCH) (b). DPCH also has a γ-relaxation process. For the α-process, the lines are fits to the VFT equation. For the β- and γ-processes, the lines are fits to the Arrhenius equation.

α-relaxation is from 220 to 247 K, with the upper limit set by crystallization. The values of the dielectric loss ε'' obtained for DPCP are consistent with a temperature-independent Kohlrausch−Williams−Watts (KWW) β parameter of 0.52. The relaxation times for each temperature are fit to the Vogel−Fulcher−Tammann (VFT) equation:

$$\log(\tau/s) = A + \frac{B}{T - T_0}$$

The VFT parameters for the α-relaxation of DPCP are fitted as $A = -17.7$, $B = 974$ K, and $T_0 = 171$ K. For the analysis below,

we make use of a dielectric estimate of T_g, determined by the temperature at which the relaxation time equals 100 s. For DPCP, this temperature is found to be 220.4 K, which is in good agreement with the T_g value of 222 K from differential scanning calorimetry (DSC).[18] The kinetic fragility index $m = [d \log \tau/d(T_g/T)]|_{\tau=100s}$ for DPCP is calculated to be 87. DPCP also exhibits a higher frequency relaxation process. Following the convention that relaxation processes are designated by their frequency ordering, we refer to this process as the β-relaxation. The β-relaxation was observed in the temperature range from 150 to 215 K; it follows the Arrhenius equation with an activation energy (E_a) of 62 kJ/mol and a prefactor of 3.8×10^{20} s^{-1}.

The dielectric results for DPCH are found in Figure 1b. As above, the values of ε'' obtained for DPCH exhibit time–temperature superposition and are consistent with a KWW β parameter of 0.52. The α-relaxation is fitted as $A = -18.5$, $B = 1160$ K, and $T_0 = 171$ K over the range of 225 to 249 K. The temperature at which $\tau_\alpha = 100$ s is determined to be 227.6 K, in reasonable agreement with the T_g value of 230 K determined by DSC.[18] The kinetic fragility parameter $m = 82$. The β-relaxation process is described by the Arrhenius equation with $E_a = 61$ kJ/mol and a prefactor of 3.0×10^{20} s^{-1}. Additionally, a γ-relaxation process was observed in DPCH with fitting parameters of $E_a = 23$ kJ/mol and a prefactor of 2.6×10^{13} s^{-1}. The dielectric loss spectra are available in the Supporting Information.

Crystal Growth Rates. The crystal growth rates u of liquid and glassy DPCP are displayed in Figure 2a. At low supercooling, near the melting temperature (T_m = 329 K), the crystal growth is limited by the thermodynamic driving force and thus the rate of growth increases with cooling. With further cooling, crystal growth rates begin to decrease as the system moves into the diffusion-controlled regime. Growth rates decrease by 6 orders of magnitude until the onset of GC growth at $T_t = 224.5$ K, 2.5 K above the DSC T_g.

The most striking aspect of the GC mode is the speed of crystal growth. An appreciation of this speed is best understood relative to the mobility of the amorphous material from which the crystals grow. In one structural relaxation time τ_α for the supercooled liquid, an active GC crystal of DPCP grows by 50 molecular layers at T_t; a few K below T_t, where $\tau_\alpha = 100$ s, 800 molecular layers are added in each structural relaxation time. In contrast, in the diffusion-controlled regime, one structural relaxation time τ_α results in the addition of 10^{-2} to 10^{-5} molecular layers to a DPCP crystal. Other GC systems including DPCH and OTP behave in a similar manner.[22,23]

Crystal growth rates versus temperature for DPCH are plotted in Figure 2b. Adjusting for the different physical properties of the material[18] (T_g = 230 K and T_m = 317 K), DPCH behaves similarly to DPCP. T_t for DPCH is found to be 233 K and is above the DSC T_g by an interval similar to that observed for DPCP (~3 K in both cases).

For both DPCH and DPCP, the onset of GC growth was marked by a change in crystal morphology, from elongated crystals to a fine-grained structure. A similar change in morphology has been noted for OTP.[20,24] A noteworthy aspect of the GC growth in DPCP was a transient growth rate which was faster than the steady-state GC growth that we report in Figure 2 (see Supporting Information).

Some GC active systems have been observed to produce fast growing crystalline fibers at temperatures near and above the GC transition temperature T_t. These fibers are notable as they
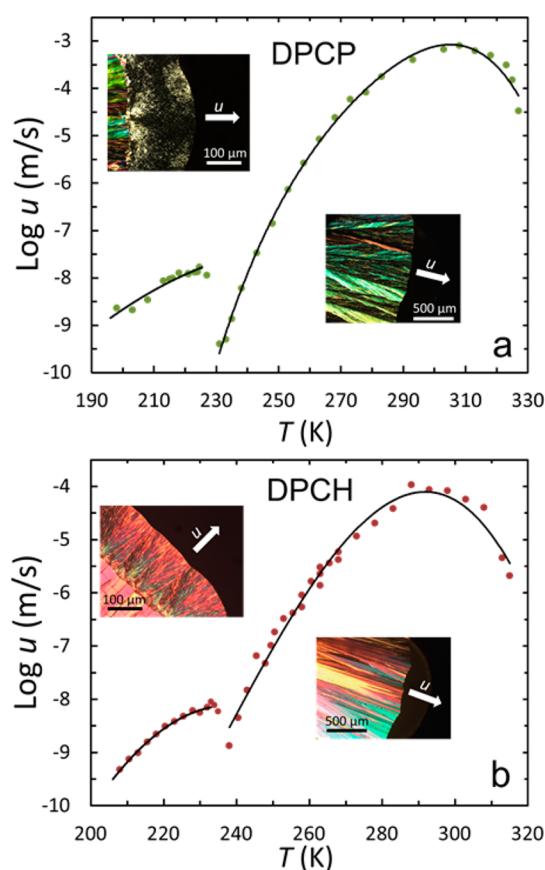

Figure 2. Crystal growth rates for (a) DPCP and (b) DPCH; lines to guide eye. Pictures show typical growth morphologies for GC growth (left) and diffusion-controlled growth (right).

are faster than diffusion-controlled growth and can persist to higher temperatures (1.15 T_g) than GC growth.[20,23] Fiber growth was observed at 227 and 228 K for DPCP and at 235 K for DPCH.

The crystal growth rates for the related molecules of 1,2-diphenylcyclobutene and 1,2-diphenylcycloheptene were also explored, and these results are available in the Supporting Information. The liquid dynamics of these two molecules could not be characterized due to crystallization.

■ DISCUSSION

Liquid Dynamics. In addition to the similarity in molecular structure of DPCH, DPCP, and OTP, we find that the structural relaxation processes of these three supercooled liquids are similar after scaling the temperature by T_g. Figure 3a plots τ_α as solid lines for the three liquids as a function of temperature (scaled to the temperature where $\tau_\alpha = 100$ s). Over a wide range of scaled temperature, the structural relaxation times of the three liquids are nearly identical. The full widths at half-maximum of the dielectric loss spectra on a log frequency scale for the three liquids are also similar (KWW $\beta = 0.50$ for OTP[25] vs $\beta = 0.52$ for the two cyclic stilbenes), indicative of very similar distributions of relaxation times. In addition, the three liquids give rise to dielectric signals of small amplitude, indicating that all three liquids are quite nonpolar. Below we make use of the similar structure and dynamics of these systems to probe the factors that influence GC growth.

α-Process, β-Process, and GC Growth. We find a strong correlation between the α relaxation process and the onset of
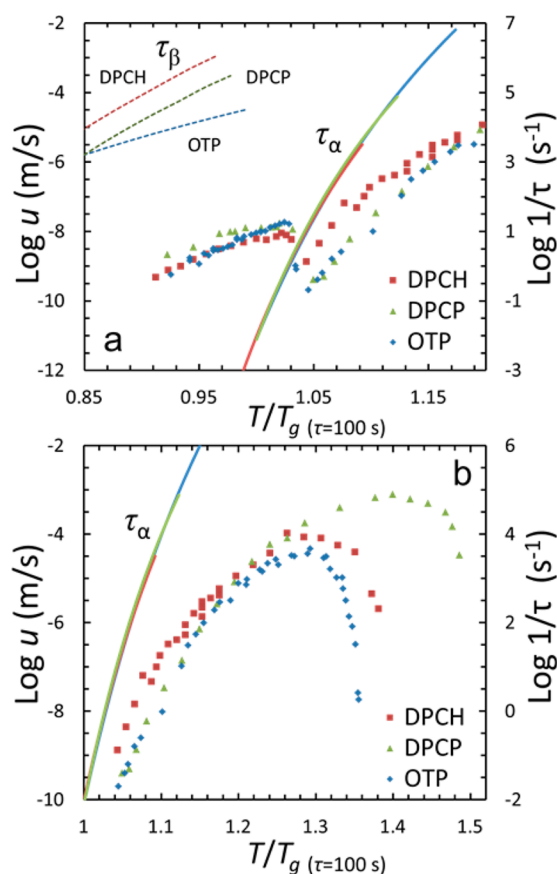
Figure 3. Crystal growth rates and dielectric relaxation times for DPCP, DPCH, and OTP. The temperature has been scaled by the dielectric glass transition temperature (the temperature where τ_α =100 s). For OTP, values of u are from refs 13 and 26, values of τ_α are from ref 25, and values for the β-relaxation are from ref 27. Panel (a) shows the transition from diffusion-controlled growth to GC growth while panel (b) shows the transition from thermodynamically controlled to diffusion-controlled crystal growth.

GC growth. A comparison of crystal growth rates for DPCP, DPCH, and OTP is shown in Figure 3a along with the structural relaxation times. In this format, it is apparent that the GC process emerges in all three liquids at approximately the same α-relaxation time. Furthermore, the temperature scaling that superposes the structural relaxation times also superposes the GC crystal growth rates to a first approximation. This superposition does not mean that the structural relaxation process supports GC growth. It is already established that the time scale of GC growth is far shorter than τ_α and that the two processes have very different activation energies.[22] The significant observation here is that the onset temperature for the GC process is not arbitrary. Rather, for these three liquids with similar molecular structure, GC growth is activated as liquid mobility falls below the same threshold value of τ_α. To glean further insight into the onset condition for GC growth, it would be useful to systematically examine the onset of GC growth and structural relaxation data for all available data on GC active systems. Additionally, it would be useful to perform the same analysis using diffusivity as the measure of liquid mobility, given that this property is known to decouple from the structural relaxation time and is a better predictor of crystal growth rates in the mobility-controlled regime.[12] Unfortunately, such data are not available for DPCP and DPCH.

If the α process is too slow to support GC growth, it is worthwhile to inquire whether another molecular relaxation process can serve this role. This inquiry need not be fruitful since molecular motions at the crystal/liquid interface may differ from those in the bulk liquid. But to the extent a surrogate relaxation process can be discovered, it will prove useful for predicting the kinetics of GC growth. The β-relaxation process, also shown in Figure 3a, has been considered as possibly providing the molecular motions that support GC growth.[28] This view is reasonable in that the β-process persists below T_g at rates fast enough to support GC growth. On the basis of Figure 3a, we can compare activation energies for GC growth and the β-relaxation processes for these three systems. For DPCP, the activation energy for GC growth ($E_{a,GC}$) is 30 kJ/mol and the activation energy of the β-process ($E_{a,\beta}$) is 62 kJ/mol, for DPCH $E_{a,GC}$ = 45 kJ/mol and $E_{a,\beta}$ = 61 kJ/mol, and for OTP $E_{a,GC}$ = 65 kJ/mol[20] and $E_{a,\beta}$ = 36 kJ/mol[27] or 48 kJ/mol.[29] While the activation energies for GC growth and the β-relaxation process are broadly similar for each system (within a factor of 2), for DPCP and DPCH the β-process has the stronger temperature dependence while it has the weaker temperature dependence for OTP. As such, these data suggest no compelling connection between the observed β-relaxation processes and the kinetic origin of GC growth. Other arguments against the β-process as the underlying mechanism for GC growth have been made elsewhere.[20,22]

Crystal Growth at Temperatures above the GC Regime. We first comment on the maximum crystal growth rates observed for each supercooled liquid. Figure 3b compares the crystal growth rates for DPCP, DPCH, and OTP in the temperature regime above T_t. The maximum growth rate for DPCP is faster than either OTP or DPCH by an order of magnitude. This behavior can be qualitatively understood on the basis of the Wilson−Frenkel equation:[9,10]

$$u = u_{kin}\left[1 - \exp\left(-\frac{\Delta G}{RT}\right)\right] \approx u_{kin}\left[1 - \exp\left(-\frac{\Delta S_m \Delta T}{RT}\right)\right]$$

Here the overall rate of crystal growth is represented as the product of a kinetic crystal growth rate u_{kin} and a term that accounts for the thermodynamic driving force. For the thermodynamic component, ΔG is the change in free energy between the liquid and crystalline states, ΔS_m is the entropy difference at melting, ΔT the amount of supercooling, and R the universal gas constant. At fixed undercooling ΔT, the thermodynamic driving forces for crystallization of DPCP, DPCH, and OTP are quite similar, because their values of ΔS_m are similar, 66, 54, and 62 J/(mol K), respectively.[18] In the Wilson−Frenkel framework, u_{kin} is expected to be a very similar function of scaled temperature for the three systems, because of their nearly identical α-relaxation times.

Within the framework of the Wilson−Frenkel equation, the only significant difference between DPCP, DPCH, and OTP is the ratio of the glass transition temperature and melting point T_g/T_m, and this qualitatively explains the larger maximum crystal growth rate of DPCP. (T_g/T_m is 0.68 for DPCP and 0.73 and 0.75 for DPCH and OTP, respectively.[18]) For DPCP at temperatures near 1.4 T_g, the thermodynamic driving force for crystal growth is large and the kinetic resistance to crystal growth is quite small. For DPCH and OTP, in contrast, a large thermodynamic driving force is only acquired at a lower temperature where the α-relaxation time is longer and therefore the kinetic constraints to crystal growth are more pronounced.

This argument is closely connected to the work of Ping et al., who noted that T_g/T_m for the cyclic stilbenes and OTP provided an excellent correlation with glass forming ability, as gauged by the critical cooling rate.[18]

We also comment on the crystal growth rates in the diffusion-controlled regime, seen in Figure 3a. The crystal growth rates for DPCH are faster than either OTP or DPCP by an order of magnitude. This feature is not anticipated by the Wilson−Frenkel model of growth. Wilson−Frenkel would predict essentially identical crystal growth rates on the basis of nearly identical kinetic resistance to crystal growth, because of the very similar α-relaxation times for these three molecular liquids. (In this temperature regime, the thermodynamic driving force has only a small influence on crystal growth rates.) A standard revision of the Wilson−Frenkel model is to introduce a multiplicative factor that describes the fraction of sites on the crystal surface that are active for growth.[19] Allowing this fraction to be an order of magnitude larger for DPCH than the other two systems would rationalize the observed behavior.

Figure 4 shows $\log u_{kin}$ versus $\log \tau_\alpha$ for DPCP, DPCH, and OTP; u_{kin} was calculated from the experimental growth rates
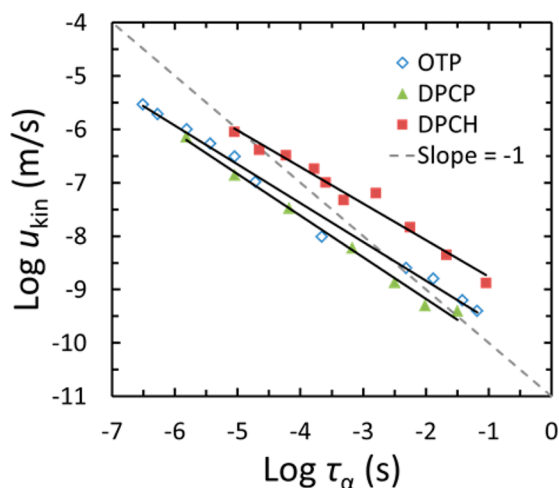

Figure 4. Kinetic component of the crystal growth rate u_{kin} plotted against the α-relaxation time. All three molecules demonstrate a power law relationship with $u_{kin} \propto \tau_\alpha^{-\xi}$ and $\xi \approx 0.7$. OTP: τ_α from ref 25, u from refs 13 and 26.

using the Wilson−Frenkel equation. The linearity shown by the experimental data in Figure 4 reveals the power law relationship: $u_{kin} \propto \tau_\alpha^{-\xi}$. DPCP, DPCH, and OTP yield ξ values of 0.78, 0.69, and 0.73 respectively. These values of ξ are in reasonable agreement with liquids of similar fragility,[19] if we note that τ_α scales nearly linearly with viscosity for supercooled organic liquids.[12,30] The authors of ref 19 have argued that the weaker temperature dependence of crystal growth rates, relative to the structural relaxation time, is a manifestation of spatially heterogeneous dynamics in deeply supercooled liquids. The weaker temperature dependence for crystal growth plays a significant role in the failure of the Wilson−Frenkel expression in the deeply supercooled regime. For example, the crystal growth of DPCH is predicted to be slower by 3 orders of magnitude than the experimental result. More information on this point is available in the Supporting Information.

Role of Crystal Structure in GC Growth. Previous work on ROY,[15] a highly polymorphic system, has demonstrated that some polymorphs support GC growth while others do not. A key feature separating the GC active polymorphs from those that are not GC active is their crystal packing. For ROY, crystal structures with more isotropic packing showed GC growth while polymorphs with anisotropic packing did not. The authors of ref 15 argued that the GC-active crystal structures were more similar in molecular packing to the supercooled liquid and glass of ROY and that this similarity allowed a facile transition into the crystalline state. In contrast, for polymorphs with packing dissimilar to the liquid, significant translational reorganization of molecules would be required for crystal growth, and such motion is presumably too slow to support GC growth.

We can test the possible role of crystal packing in enabling GC growth for DPCP, DPCH, and OTP. The radial distribution functions for molecular centers of mass in the three crystal structures are displayed in Figure 5. By this
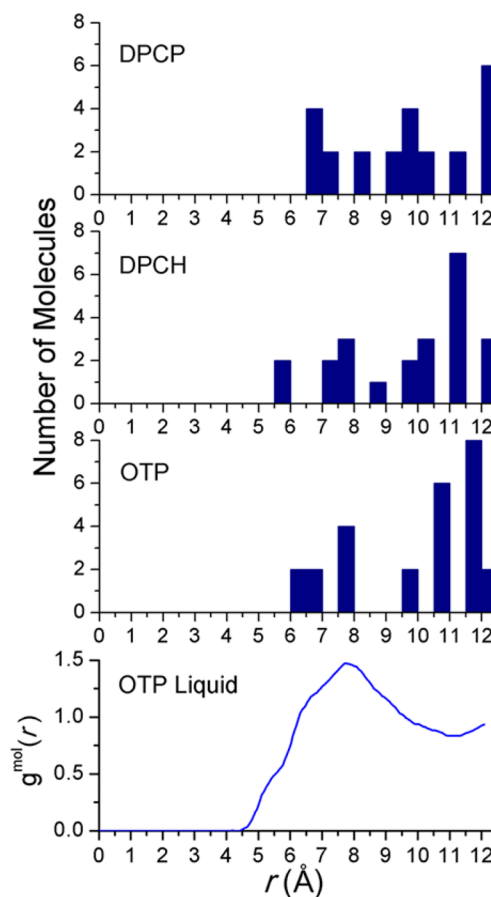

Figure 5. Center of mass radial distribution functions for DPCP, DPCH, and OTP crystals (top three panels) and the center of mass distribution function for liquid OTP from simulation (bottom panel), ref 31. The top three panels are calculated from crystal structure data for DPCP, DPCH, and OTP (refs 32 33, and 34, respectively).

measure, the crystal packing for all three molecules is quite similar, with the closest approach between the centers of mass of two neighbors being in the range of 5.5−6.5 Å in all cases. Also shown in Figure 5 is the radial distribution function for liquid OTP as determined from molecular simulation by Mossa et al.[31] The radial distribution functions of liquid and crystalline OTP are similar. Note in particular the presence of a shoulder and peak in the liquid distribution function at positions of neighbor distances in the OTP crystal. While this evaluation of

packing is qualitative, a comparison with the ROY system supports the view that all the packing arrangements shown in Figure 5 are similar; for ROY, larger changes in center of mass distributions (particularly the appearance of molecular pairs with smaller center of mass distances) distinguished GC-active polymorphs from GC-inactive polymorphs.[15]

For OTP, these results support the hypothesis that similar packing in the liquid and crystal enables GC growth. Although molecular dynamics simulations of DPCP and DPCH are not currently available, we expect that packing in these liquids is very similar to packing in liquid OTP, given their similar molecular structures. If this is correct, then liquid and crystal packing are similar for both DPCP and DPCH, consistent with the idea that this is a requirement for GC growth. Clearly it would be beneficial if the liquid state packing of DPCP and DPCH could be examined in molecular dynamics simulations. This would allow a detailed comparison of the liquid and crystal packing that could go beyond center of mass distributions to consider the relative orientations of molecules in the liquid and crystal.

CONCLUSION

In this study we present the liquid dynamics and crystal growth kinetics of 1,2-diphenylcyclopentene (DPCP) and 1,2-diphenylcyclohexene (DPCH). These molecules have structures similar to the well-studied glassformer o-terphenyl (OTP) and are found to have dynamics typical of fragile glassformers. Rapid glass crystallization, known as GC (glass to crystal) growth, is observed for both systems, and this observation demonstrates that a crystal structure with liquid-like packing may be a requirement for supporting GC growth. In the diffusion-controlled region of crystal growth, near T_g, both systems exhibit a power law relationship between the crystal growth rate and the structural relaxation time, $u_{kin} \propto \tau_\alpha^{-\xi}$, with values of ξ near 0.7.

Significant questions remain about the GC mode of crystal growth. We observed that crystal growth rates for DPCP, DPCH, and OTP are very similar in the GC mode, after scaling the temperature based on τ_α. While this argues for an important role for the α-relaxation process in determining the onset of GC growth, the α-process is far too slow to provide the motions necessary to support GC growth. When GC growth is compared to the faster β-processes observed here, no clear connection emerges. At this time the mechanism that supports GC growth at such a rapid rate remains uncertain along with the origins of fiber growth. Further study is needed to fully elucidate this phenomenon.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Dielectric data, crystal growth details, and crystal growth rate predictions. This material is available free of charge via the Internet at http://pubs.acs.org.

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