Glassy dynamics of crystallite formation: The role of covalent bonds

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We examine nonequilibrium features of collapse behavior in model polymers with competing crystallization and glass transitions using extensive molecular dynamics simulations. By comparing to “colloidal” systems with no covalent bonds but the same non-bonded interactions, we find three principal results: (i) Tangent-sphere polymers and colloids, in the equilibrium-crystallite phase, have nearly identical static properties when the temperature $T$ is scaled by the crystallization temperature $T_{\text{cryst}}$; (ii) Qualitative features of nonequilibrium relaxation below $T_{\text{cryst}}$, measured by the evolution of local structural properties (such as the number of contacts) toward equilibrium crystallites, are the same for polymers and colloids; and (iii) Significant quantitative differences in rearrangements in polymeric and colloidal crystallites, in both far-from equilibrium and near-equilibrium systems, can be understood in terms of chain connectivity. These results have important implications for understanding slow relaxation processes in collapsed polymers, partially folded, misfolded, and intrinsically disordered proteins.

1 Introduction

Collapse transitions of single chain polymers induced by changing control parameters such as temperature or solvent quality yield rich nonequilibrium behavior when the rate at which these control parameters are changed exceeds characteristic (slow) dynamical rates. Investigating the glassy dynamics of polymer collapse is important for understanding e.g. crystallization kinetics and protein misfolding, yet the majority of studies have focused on equilibrium behavior. In this manuscript, we characterize the nonequilibrium and near-equilibrium collapse and crystallization dynamics of single flexible polymer chains.

We employ a minimal model that yields competing crystallization and glass transitions. Monomers are modeled as monodisperse tangent spheres with hard-core-like repulsive and short-range attractive interactions. Recent studies\textsuperscript{1,2} have shown that in equilibrium, model polymers with narrow square-well interactions exhibit direct “all-or-nothing” crystallization transitions that mimic the discrete folding transition observed in experimental studies of proteins.\textsuperscript{3} Short-range attractions also give rise to degenerate, competing ground states, which kinetically hinder collapse to equilibrium crystallites. The associated rugged energy landscapes are believed to control the behavior of intrinsically disordered proteins.\textsuperscript{4,5}

A novel aspect of our work is quantitative comparison of polymer collapse dynamics to that of ‘colloidal’ systems with the same secondary interactions but no covalent bonds. Polymers are distinguished from other systems by their topology; connectivity and uncrossability constraints imposed by covalent backbone bonds give rise to cooperative dynamics\textsuperscript{6} and phase transitions\textsuperscript{7} not present in nonpolymeric materials. Our choice of tangent monodisperse spheres yields identical low-energy states for polymers and colloids, but (because of the covalent backbone) very different free energy landscapes.\textsuperscript{8} This greatly facilitates a robust comparison of crystallite formation and growth dynamics that isolates the role of topology and allows us to isolate and quantify the contributions of the covalent bonds and chain uncrossability to cooperative rearrangements and slow dynamics during collapse. We perform this comparison using extensive molecular dynamics simulations of thermal-quench-rate-dependent collapse and post-quench growth of polymeric and colloidal crystallites.

Figure 1 depicts rate-dependent collapse behavior of systems interacting via hard-core-like repulsions and short-range attractions.\textsuperscript{9} In the limit of slow quench rates $|\dot{T}| < |\dot{T}^*|$, where $\dot{T}^*$ is a critical quench rate, finite systems exhibit a first-order-like transition from a high-temperature “gas” (for polymers, a self-avoiding random coil) phase to crystallites. The equilibrium transition occurs if $|\dot{T}|$ is small compared to key relaxation rates, such as the crystal nucleation rate $\nu$ and rate $\gamma$ of large rearrangements in compact structures. At larger $|\dot{T}|$, systems fall out of equilibrium, and pass onto the metastable liquid branch. If $T$ becomes low enough such that $s(T) \gg |\dot{T}|$, the systems become glassy and disorder is frozen in at $T = T_{\text{glass}}$. Otherwise, systems relax towards equilibrium crystallites, as indicated by the downward arrow.

Our analyses compare collapse behavior within the framework of Fig. 1. We find that polymers and colloids behave similarly in many ways, and differences can be linked directly

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where \( \varepsilon \) is the intermonomer binding energy, \( D \) is the monomer diameter, and \( k = 1600 \varepsilon \) is the spring constant. The only difference between colloidal and polymeric interactions (inset to Fig. 2(a)) is that in polymeric systems, the monomers are linked into a linear chain connected by \( N - 1 \) permanent covalent bonds. Different values for \( r_c \) are used for covalently and noncovalently bonded monomers: \( r_c^c/D = \infty \) and \( r_c^{nc}/D = 1 + \sqrt{2} \varepsilon/k_B \), respectively.

Newton’s equations of motion are integrated using the velocity-Verlet method with a timestep \( dt = \tau/800 \), where \( m \) is the monomer mass and \( \tau = \sqrt{mD^2/\varepsilon} \). We determined that this timestep was sufficiently small by examining \( dt \)-dependence of the velocity autocorrelation function \( v_{ac}(t) \) in simulations at high temperature; no statistically significant dependence was found for \( dt \leq \tau/600 \). Below, we express length scales, energies, times, rates and temperatures in units of \( D, \varepsilon, \tau, \tau^{-1}, \) and \( \varepsilon/k_B \), respectively. The temperature \( T \) is controlled via a Langevin thermostat with damping time \( 10^3 \). A periodic cubic simulation cell with volume \( L^3 \) fixes the monomer density \( \rho \). We present results for \( \rho = 0.01 \), which is in the dilute limit.

Systems are initialized in random walk initial configurations (for polymers) and random nonoverlapping initial positions (for colloidal systems). They are then equilibrated at high temperature, \( k_B T_i/\varepsilon = 0.75 \), for times long compared to the time over which the self intermediate scattering function decays to zero. At \( T = T_i \), polymeric systems are in the good-solvent (self-avoiding coil) limit, and colloidal systems are in an ideal-gas-like state. Following equilibration, systems are thermally quenched at various rates \( \dot{T} \). In our ensemble-averaging approach, states from which thermal quenches are initiated are separated by times long compared to structural relaxation times, and thus are statistically independent.

The quenches are either continued to \( T = 0 \) or terminated at \( T = T_f < T_{cryst} \). In the latter case, we continue the runs at fixed \( T_f \). We choose \( T_f/T_{cryst} = 7/8 \) to suppress finite-\( N \) fluctuation effects associated with thermal broadening of the phase transition to crystallites, i.e. \( T_f/T_{cryst} \lesssim 1 - N^{-1/2} \), yet allow sufficiently fast relaxation to be captured within the limits of available computational resources for the \( N \) considered here (40, 100, and 250). As we simulations with physically realistic dynamics are better able to capture the complex, coordinated rearrangement events associated with the glassy dynamics of crystallization.

In our studies, both colloidal and polymeric systems consist of \( N \) identical spherical monomers that interact via the harmonic “sticky-sphere” potential shown in Fig. 2(a):

\[
U_{harm}(r) = \begin{cases} 
-\varepsilon + \frac{k}{2} \left( \frac{r}{D} - 1 \right)^2, & r < r_c \\
0, & r > r_c 
\end{cases}
\]

where \( \varepsilon \) is the intermonomer binding energy, \( D \) is the monomer diameter, and \( k = 1600 \varepsilon \) is the spring constant. The only difference between colloidal and polymeric interactions (inset to Fig. 2(a)) is that in polymeric systems, the monomers are linked into a linear chain connected by \( N - 1 \) permanent covalent bonds. Different values for \( r_c \) are used for covalently and noncovalently bonded monomers: \( r_c^c/D = \infty \) and \( r_c^{nc}/D = 1 + \sqrt{2} \varepsilon/k_B \), respectively.

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will show below, this procedure yields particularly interesting results for nonequilibrium relaxation following quenches at moderate $|\dot{T}|$. $T_J/T_{\text{cryst}} = 7/8$ is also comparable to temperatures used in many experimental and simulation studies of crystallite nucleation and growth in supercooled colloidal and polymeric systems.16,17

We will examine several order parameters to characterize nucleation, growth and rearrangements of crystallites as a function of temperature and time following thermal quenches to $T_J/T_{\text{cryst}} < 1$. These order parameters are generated from the adjacency matrix $A$; $A_{ij} = A_{ji} = 1$ when particles $i$ and $j$ are in contact, i.e. when the position vectors satisfy $|\vec{r}_i - \vec{r}_j| < r_c$, and 0 otherwise.

Our interaction potential (Eq. 1) promotes contact-dominated crystallization dynamics. For the large $k/\epsilon$ and small $r_c$ employed here, the ground states for colloidal and polymeric systems19 are simply the states that maximize the number of pair contacts $N_c = \Sigma_{j>i} A_{ij}$ for a given $N$.20 Further, our systems form crystallites possessing close-packed cores that increase in size as $T$ decreases or equilibrium is approached.20 We therefore measure the number of closed packed monomers $N_{cp} = \Sigma_i^N \delta(\Sigma_j A_{ij} - 12)$ and degree distribution $P(\eta)$, i.e. the probability for a particle to have $\eta$ contacts. Note that $\Sigma_{i=1}^{12} i P(i) = 2N_c/N$ and $P(12) = N_{cp}/N$. $P(\eta)$ contains more information than $N_c$ and $N_{cp}$ since it describes the high-$\eta$ cores of crystallites as well as their surfaces, where monomers naturally have lower $\eta$.20 We will argue below that the combination of $N_c$, $N_{cp}$ and $P(\eta)$ forms an effective set of “crystal-agnostic” order parameters (in the spirit of Rein ten Wolde et al.20).

We will also present results for the adjacency matrix autocorrelation function $P_{\text{AMAC}}(t_w, t')$ as a function of $t'$ after waiting various times $t_w$ following thermal quenches to $T_J$:

$$P_{\text{AMAC}}(t_w, t') = \left\langle \sum_{i,j>i} A_{ij}(t_w) A_{ij}(t_w + t') / \sum_{i,j>i} A_{ij}(t_w) A_{ij}(t_w) \right\rangle,$$

(2)

where the brackets indicate an ensemble average over independently prepared samples, and the total time elapsed after termination of the quench is $t = t_w + t'$. For polymers, we exclude the contributions of covalent bonds to $P_{\text{AMAC}}$ by summing over $j > i + 1$ rather than $j > i$ in Eq. 2. Both $P_{\text{AMAC}}(t')$ and the intermediate scattering function $S(q,t')$ evaluated at $qD \simeq 2\pi$ identify rearrangements of contacting neighbors, which control the slow relaxation processes in colloidal systems with competing crystallization and glass transitions.21,22 To capture the glassy dynamics, we examine systems with $t_w$ ranging over several orders of magnitude and $t' \gg t_w$.

* $P(\eta)$ is also closely related to the spectrum of eigenvalues of $A$.26 While these eigenspectra provide additional information on crystallite structure, we leave their examination for future studies of equilibrium systems.

### 3 Results

In this section, we compare the collapse and ordering dynamics of colloids and polymers using two protocols. Protocol (1) consists of decreasing the temperature from an initially high value $T_i$ to zero using a wide range of thermal quench rates $\dot{T}$. To analyze changes in structure with decreasing $T$, we measure the potential energy, $N_c$, and $N_{cp}$ over the full-range of temperature for each quench rate. Protocol (2) consists of quenching systems from $T_i$ to $T_J = (7/8)T_{\text{cryst}}$ using a range of $T$ and then monitoring structural order and rearrangement events within crystallites at $T = T_J$ as systems evolve toward equilibrium. We measure $N_c(t)$, $N_{cp}(t)$, $P(\eta; t)$ and $P_{\text{AMAC}}(t_w, t')$, to quantify evolution to more ordered states, and also perform detailed studies of crystallite rearrangements in a “pre-terminal” relaxation regime where the systems slowly approach equilibrium.

#### 3.1 Protocol 1: Thermally Quench from High to Zero $T$

**Potential Energy:** Figure 2 shows results for the scaled potential energy $U/N\epsilon$ for colloidal and polymer systems quenched from $T = T_i$ to zero. Panel (a) shows results at low $|\dot{T}|$ for system sizes ranging over a factor of six in $N$, while panel (b) shows results for $N = 100$ over a range of $|\dot{T}|$ spanning four orders of magnitude. All results are consistent with the general picture of Fig. 1 and illustrate both features common to polymers and colloids as well as differences arising from the presence of a covalent backbone.

At the lowest $|\dot{T}|$ considered ($\sim 10^{-8}$), both colloids and polymers show sharp, first-order-like transitions at corresponding $T = T_{\text{cryst}}$. Because of the narrowness of the attractive range of the potential well,12,29 no intermediate liquid state (i.e., globules in the case of polymers) appears.20,30 In both cases, as in Fig. 1, the equilibrium transitions are from gas-like states to crystallites. No significant quench rate dependence is observable for $T > T_{\text{cryst}}$, which indicates that all $|\dot{T}|$ are sufficiently low to be near-equilibrium in this high temperature regime. For $|\dot{T}| \sim 10^{-8}$, polymers and colloids have the same energy at low $T$ to within statistical noise, showing that this quench rate is slow enough to be in the near-equilibrium limit for polymers (i.e. $|\dot{T}^*| \gtrsim 10^{-8}$ for these systems.) The $N$-dependence (panel (a)) shows only quantitative rather than qualitative differences. As $N$ increases, values of $U/N\epsilon$ in the $T \rightarrow 0$ limit decrease because larger crystallites possess more interior monomers.

Compared to colloids, polymers have lower $U/N\epsilon$ for $T > T_{\text{cryst}}$ because of the permanent covalent bonds, which contribute $-k_BT/\epsilon - 1$.29 They also have higher absolute values of $T_{\text{cryst}}$ (Table 1). To zeroth order, $T_{\text{cryst}}/T_{\text{cryst}} \approx 3/2$, a ratio which can be explained by a simple degree-of-freedom counting argument: while colloids have $3N - 6$ nontrivial

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degrees of freedom, the stiff covalent bonds in polymers act like holonomic constraints, reducing the effective dimensionality of their phase space to $2N - 5$ so that $T_{\text{cryst}} = [(3N - 6)/(2N - 5)]T_{\text{coll}} \approx 3/2$. This observation helps motivate our (protocol 2) studies comparing relaxation of polymeric and colloidal crystallites at equal values of $T/T_{\text{cryst}}$ in terms of their different free energy landscapes.

Table 1 Dependence of $T_{\text{cryst}}$ on $N$ and topology. Our data are consistent with detailed analyses predicting $O(N^{-1/3})$ finite-size corrections to $T_{\text{cryst}}$.

| $N$  | $T_{\text{coll}}$ | $T_{\text{pol}}$ | $T_{\text{pol}}/T_{\text{coll}}$ |
|------|------------------|------------------|-------------------------------|
| 40   | 0.237            | 0.342            | 1.44                          |
| 100  | 0.240            | 0.375            | 1.56                          |
| 250  | 0.239            | 0.383            | 1.60                          |

Below $T_{\text{cryst}}$, dramatic quench rate dependence appears. Consistent with the general picture of Fig. 1 with increasing $|\dot{T}|$, the $T$-dependent potential energy increases relative to the equilibrium-crystal limit. Figure 2(b) shows results for $N = 100$. Similar trends are observed for the other $N$ considered, with the main difference being that $|\dot{T}^*|$ increases and rate effects for $|\dot{T}| > |\dot{T}^*|$ become more dramatic with increasing $N$.

Contact number: We now discuss the temperature dependence of local measures of structure during quenches. Figure 3 shows $N_c(T)$ and $N_{cp}(T)$ plotted against $T$ and $T/T_{\text{cryst}}$ for the same systems analyzed in Fig 2(b). $N_c/N$ and $N_{cp}/N$ are particularly sensitive measures of crystallite equilibration. They increase monotonically with decreasing $|\dot{T}|$, but the variations with rate are different for polymers and colloids. For fast quenches, polymers are more efficient crystal formers due to topological connectivity and the resultant cooperative dynamics. An example of a cooperative polymer collapse mechanism not found in colloids is “chain pull-in”: a nucleus forms between chemically nearby monomers, and covalent bonds pull in segments that are chemically adjacent to the nucleus. However, as exemplified by the $|\dot{T}| = 10^{-4}$ results, this mechanism produces only small ordered cores with highly disordered exteriors. Note that for the fastest quench rates, the collapsed structures possess $N_c/N \geq 3$, which is the minimal number of contacts for mechanical stability and corresponds to the isostaticity threshold shown in panel (a).

In Fig. 3(a), we show that $|\partial N_c/\partial T| \rightarrow 0$ at a noticeably higher $T$ for polymers than colloids, which indicates that large structural rearrangements cease, and polymers possess a higher $T_{\text{glass}}$ than colloids. Polymer chain backbones follow tortuous paths through the interior of collapsed states and chain uncrossability suppresses large rearrangements, so a higher $T_{\text{glass}}$ is consistent with the expected slower relaxation dynamics for polymer crystallites.
3.2 Protocol 2: Thermally quench from high $T$ to $T_f < T_{\text{cryst}}$ and monitor relaxation at fixed $T_f$

As shown in Table 2, polymeric and colloidal crystallites of the same $N$ have nearly equal values of both $\langle N_{\text{coll}}/N \rangle$ and $\langle N_{\text{pol}}/N \rangle$ at $T_f = (7/8)T_{\text{cryst}}$. They also have similar structure (i.e. $P(\eta)$; cf. Fig. 5). This helps establish that comparison of relaxation dynamics in polymeric and colloidal crystallites at fixed $T_f$ is a reasonable approach to isolating the

† Collapse worsens only slightly with increasing $N$, indicating that $|\dot{T}^*|$ increases slowly with $N$. Precise calculation of $|\dot{T}^*(N)|$ is outside the scope of this study, but more quantitative results for the $N$-dependence of characteristic relaxation times is given in Section 3.2.

‡ This variation is significant when one considers that the isostatic value $\langle N_{\text{coll}}/N \rangle = 3$ can be attained by systems as small as $N = 16$, while the limiting value for infinite $N$ (corresponding to defect-free close-packed crystals) is $\langle N_{\text{col}}/N \rangle = 6$.
role played by topology in controlling the approach of crystallites to equilibrium.

We now examine systems quenched at different rates and monitor their evolution as a function of time $t$ following termination of the quenches to $T_f$. Measures such as the evolution of contact order and several measures of local and nonlocal rearrangements after different waiting times $t_w$ show that polymeric crystallites possess significantly slower long-time relaxation dynamics at equal values of $T/T_{cryst}$ despite their similar structure. Studies of system size dependence show that this “topological” slowdown is related to the more correlated rearrangements imposed by uncrossable covalent backbones, and strengthens with increasing $N$.

**Contact number:** Fig. 4 shows the evolution of $\delta N_c$, $\langle N_c \rangle$, and $\langle N_{cp} \rangle$ in polymeric and colloidal systems as a function of time $t$ following thermal quenches to $T_f$ at rates $|\dot{T}| = 10^{-6}$ and $10^{-7}$. $\delta N_c$ is the root-mean-square fluctuation in the number of contacts averaged over an ensemble of collapse trajectories. The strong increase in $\langle N_c \rangle$ and $\langle N_{cp} \rangle$ and drop in $\delta N_c$ after $t \approx 10^5$ for $|\dot{T}| = 10^{-6}$ in Fig. 4(a) suggests that the crystal nucleation rate for colloids is $r_c \approx 10^{-5}$. In contrast, polymers do not show a rapid increase in the number of contacts (or concomitant decrease in the contact number fluctuations) at these thermal quench rates, showing that the crystal nucleation rate for ($N = 100$) polymers is $r_p \gtrsim 10^{-5}$.

As shown in Fig. 4(b) and (c), at long times $t > 10^6$ both polymeric and colloidal systems show evidence of logarithmic relaxation toward equilibrium. The logarithmic increase in $\langle N_c(t) \rangle$ and $\langle N_{cp}(t) \rangle$ is consistent with thermal activation over large energy barriers and transitions between metastable, globule-like states and near-equilibrium crystallites. Relaxation is also slowed by the increasing mechanical rigidity associated with increasing $N_c$. The approach to equilibrium occurs through thermally-activated rearrangements of particles associated with “soft modes” (cf. Figs. 7-8), which are known to play a significant role in structural and stress relaxation in supercooled liquids. At larger $t$, the slopes (indicated by green solid lines) are clearly larger for colloids than for polymers; values of $\partial <N_c>/\partial \ln_{10} t$ and $\partial <N_{cp}>/\partial \ln_{10} t$ fit over the range $10^{6.5} \leq t \leq 10^7$ are given in Table 3.

For $t > 10^7$, values of $\partial <N_c(t)>/\partial \log_{10}(t)$ and $\partial <N_{cp}(t)>/\partial \log_{10}(t)$ show that the approach to the ergodic limit can be clearly seen in the vanishing of “history” dependence for systems quenched at different rates, i.e. curves for different $\dot{T}$ overlap at large $t$. In contrast, for polymers, history dependence and faster logarithmic relaxation persist up to the maximum time $t = 5 \cdot 10^7$. This shows that polymers possess slower characteristic relaxation rates $s_{slow}$ at the same value of $T/T_{cryst}$ even though the crystallites are less mechanically rigid (since they have fewer contacts and are...
at higher absolute $T$).

While observation of the crossover into this terminal relaxation regime for polymers with $N = 100$ and $N = 250$ monomers is made unfeasible by the limitations of current computer power, in this paper we are primarily concerned with the nonequilibrium dynamics of crystallization and the logarithmic “pre-terminal” relaxation regime of crystallite growth. We now analyze the role of topology on relaxation dynamics within the pre-terminal regime by examining the evolution of more detailed measures of crystalline order.

![Graph](image)

**Fig. 5** Evolution of degree distributions $P(\eta)$. (a) $P(\eta)$ after $|T| = 10^{-6}$ quenches to $T_f$. Curves show data averaged over times $0 \leq t \leq 10^5$ for colloids (dash-dotted) and polymers (dashed) and $0.999 \cdot 10^7 \leq t \leq 10^7$ (colloids; light solid, polymers; heavy solid). Solid circles show results averaged over the 6 distinct $N = 100$ Barlow packings. Panel (b) shows $\Delta P(\eta)$, obtained by subtracting the small-$t$ data shown in panel (a) from large-$t$ data for colloids (lighter blue line) and polymers (heavier red line). Inset: A common five-fold symmetric structure present on the surface of nonequilibrium crystallites. The green monomer has $\eta = 5$.

**Degrees distribution:** Figure 5 shows results for the evolution of $P(\eta)$ following $|T| = 10^{-6}$ quenches. Polymeric and colloidal crystallites have similar degree distributions for intermediate and high $\eta$, indicating the crystallites’ inner cores are similarly structured. However, covalent backbones produce greater differences at crystallite surfaces. Polymer topology requires $\eta \geq 2$ for chemically interior monomers and $\eta \geq 1$ for chain ends, while monomers in colloidal systems can have any degree of connectivity consistent with steric constraints (here, $0 \leq \eta \leq 12$). Because of this difference in connectivity, polymer crystallites include a higher fraction of monomers with $2 \leq \eta \leq 4$ (panel (a)); this difference strengthens as $t$ increases and systems approach equilibrium.

Panel (b) shows $\Delta P(\eta) = P(\eta; t = 10^7) - P(\eta; t = 0)$ to highlight the changes in $P(\eta; t)$ over an interval $\Delta t = 10^7$ following the end of the quench to $T_f$. Notable features common to colloidal and polymeric crystallites and depicted more clearly than in panel (a) include sharply negative $\Delta P(\eta)$ associated with the annealing out of 5-fold symmetric structures that tend to form on the surface of metastable crystallites (see inset), and sharply negative $\Delta P(\eta)$ associated with annealing out of defects within crystallite cores. The latter process is closely associated with the increase in $\langle N_{cp}(t) \rangle$ shown in Fig. 4. However, the key result shown here is that changes in $P(\eta)$ are uniformly smaller for polymers despite the higher absolute $T$.

While the equilibrium $P(\eta)$ distribution is difficult to calculate for large $N$ without resorting to advanced Monte Carlo techniques, one measure of evolving crystalline order in our systems can be obtained by comparing $P(\eta; t)$ to that of a known reference system. Barlow packings are hard-sphere packings composed of layered hexagonal-close-packed planes; their three-dimensional order may be fcc, hcp, or mixed fcc/hcp, but they possess no defects (e.g. stack faults). These are “reference” low energy structures for our model in the limit of steep hard-core repulsions and short-range attractions. The solid circles in Fig. 5(a) show $P(\eta)$ averaged over the six $N = 100$ Barlow packings.

Our simulation data show that crystallites at the end of the pre-terminal relaxation regime possess Barlow-like order. Interestingly, $\langle N_c \rangle$ is slightly higher (Fig. 4) in the simulated systems than in the Barlow packings ($\langle N_c^{\text{Barlow}} \rangle = 421$), while values of $P(12) = \langle N_{cp} \rangle / N$ are similar. These effects are attributable to finite temperature, stiffness of core repulsions and range of attractive interactions. Other differences between our systems and Barlow packings are attributable to small deviations from equilibrium, the fact that our crystallites may be stack-faulted, and (for polymers) entropic factors such as blocking. That the above complexity can be understood by examining $N_c$, $N_{cp}$, and $P(\eta)$ shows that this combination of metrics constitutes an effective “crystal-agnostic” measure of order.

In the above protocol 2 subsections, we have focused on results for $N = 100$. System size effects are minor, e.g. slower logarithmic growth of crystalline order with increasing $N$ and shift of $P(\eta)$ towards higher $\eta$. Examining rear-
Arrangements within crystallites provides additional insight into \(N\)- and topology-dependent effects on the glassy dynamics of crystallite formation and is discussed in the following subsections.

**Adjacency matrix autocorrelation function:** Next we examine the decorrelation of contacts between neighboring particles during the approach to equilibrium at \(T_f = (7/8)T_{cryst}\). We first examine effects of quench rate and waiting time on \(N = 100\) systems, and then examine \(N\)-dependence for evolution following slow quenches. The adjacency matrix autocorrelation function \(P_{AMAC}(t_w, t')\) displays several important features (Fig. 6):

(i): Polymeric rearrangement events are more frequent at low \(t'\) because of the higher absolute \(T\). However, rearrangements are slower at large \(t'\) despite the higher absolute \(T\). The slower decay arises from the covalent bonds in polymers that restrict the motion of monomer \(i\) to the plane tangent to the vector \(\vec{r}_{i+1} - \vec{r}_{i-1}\). Although contributions from permanent covalent bond contacts are excluded from the definition of \(P_{AMAC}(t_w, t')\), in compact crystallites connectivity to chemically distant monomers produces long-range suppression of contact-breaking.

(ii): Following the \(|\dot{T}| = 10^{-6}\) thermal quenches, \(P_{AMAC}(t_w, t')\) for both polymers and colloids display strong \(t_w\)-dependence as shown in Fig. 6(a). We find an increase in the length and height of the low-\(t'\) “plateau” near \(P_{AMAC}(t_w, t') \approx 0.95\) with increasing \(t_w\), similar to the behavior of the plateau in \(S(q, t_w, t')\) during the aging process in structural glasses.\(^{27}\) Aging effects are stronger for colloids than for polymers because colloids are further from equilibrium at the termination of the quenches (Fig. 4(a)).

(iii): For slower thermal quenches (\(|\dot{T}| = 10^{-7}\); Fig. 6(b)), similar but much weaker aging effects are present. Results for \(t_w = 0\) and \(t_w = 10^5\) are indistinguishable to within statistical uncertainties for both polymers and colloids. Aging is delayed in part because the additional time to quench from \(T_{cryst}\) to \(T_f\) provided by the factor of 10 decrease in quench rate is larger than \(r_{c}^{-1}/\dot{r}_c^{-1} \sim 10^2\) and \(r_{p}^{-1}/\dot{r}_p^{-1} > 10^5\) (Fig. 4(a)), and in part because for \(t_w \geq 10^{6.5}\) systems have crossed into the preterminal (logarithmic) relaxation regime at \(t' = t - t_w = 0\).

Both polymer and colloidal crystallites continue to slowly add contacts and close-packed monomers, and the \(t_w\)-dependence should not vanish until equilibrium values of \(\langle N_c \rangle\) and \(\langle N_{cp} \rangle\) are reached.

(iv): At large \(t'\), the adjacency matrix autocorrelation function decays logarithmically. The crossover to logarithmic decay of \(P_{AMAC}(t_w, t')\) corresponds to the pre-terminal regime of logarithmic growth of \(\langle N_c \rangle\) and \(\langle N_{cp} \rangle\) (Fig. 4(b) and (c)).

\(^{1}\)This could be examined quantitatively by excluding successively more distant chemical neighbors (e.g. 2nd nearest, 3rd nearest), and by considering only chemically interior sections of polymers. A detailed analysis is left for future studies of near-equilibrium and equilibrium systems.

For colloids and small \(t_w\), a decrease in the slope of this logarithmic decay corresponding to crossover into the terminal re-
laxation regime is indicated by the + symbol in Fig. 5b). No such change in slope occurs for polymers over the same range of \( t' \). This is consistent with the idea that local relaxations in polymers are slower due to chain-connectivity constraints on rearrangements.

\((\nu):\) Figure 5c illustrates the variation of \( P_{\text{AMAC}}(t_w = 0; t') \) with \( N \) for slowly quenched systems. Characteristic contact decorrelation rate \( s_{\text{cont}} \) decrease sharply with increasing \( N \); for example, the low-\( t' \) plateau lengths with increasing \( N \), and the \( t' \) at which \( P_{\text{AMAC}} = 0.8 \) is 2-3 orders of magnitude greater for \( N = 250 \) than for \( N = 40 \). Since this \( N \)-dependent decrease in \( s_{\text{cont}} \) is similar for polymeric and colloidal crystallites (which, as we have shown, possess similar structure), we attribute it to the increasing contribution of crystallite cores where reneging dynamics are slow because \( \eta \) is high and particles are more sterically constrained. Similarities and differences between polymeric and colloidal results are consistent with those expected from (i). For all \( N \), as in panels (a-b), polymers relax faster than colloids at low \( t' \) because \( T_f = (7/8)T_{\text{crys}} \) is higher, and slower at large \( t' \) because of topologically restricted rearrangement (cf. Figs. 7-8). Both the “crossover” \( t' \) at which \( P_{\text{AMAC}}^\text{pol} = P_{\text{AMAC}}^\text{col} \) and the ratio \( P_{\text{AMAC}}^\text{pol}/P_{\text{AMAC}}^\text{col} \) beyond this crossover time increase with increasing \( N \).

In this paper we focus on the glassy dynamics of crystallite formation (where about half of the contacts existing at the termination of the quench have not been broken), not complete reorganization. Below, we show that there are significant differences between large-scale polymeric and colloidal rearrangements in this regime. In the remainder of this section, we will focus on \( N = 100 \) collapsed states generated using protocol 2 with thermal quench rate \( |\dot{T}| = 10^{-7} \).

**Statistical comparison of rearrangements in polymeric and colloidal crystallites:** We describe rearrangement events using the two-dimensional parameter space \((\Delta N_c, N_{cp})\), where tangent-sticky-sphere polymers and colloids have the same inherent structures.\[^1\] In Fig. 7 we show the probability distribution \( P(\Delta N_c, N_{cp}) \) for crystallite rearrangements to add \( \Delta N_c \) contacts and \( \Delta N_{cp} \) close-packed particles in crystallites over time intervals \( \Delta t = 10^2 \). Results are calculated for the range \( 10^{6.5} \leq t \leq 10^7 \) where both colloids and polymers are in the preterminal relaxation regime. \( P(\Delta N_c, \Delta N_{cp}) \) is proportional to the integrated rate

\[
R(\Delta N_c, \Delta N_{cp}) = \int \int s(\Delta N_c, \Delta N_{cp}, N^0_c, N^0_{cp}) dN^0_c dN^0_{cp}
\]

for all transitions that add \( \Delta N_c \) contacts and \( \Delta N_{cp} \) close-packed particles in crystallites originally possessing \( N^0_c \) con-

\[^1\] Note that for the physically reasonable values \( m = 10^{-24} \text{kg}, D = 1 \text{nm}, \) and \( \epsilon \approx 10 \text{keV} \) at room temperature, \( \tau \approx 5 \text{ps}, \) and timescales \( \sim \Delta t \) can be probed by neutron spin echo experiments, e.g. for the purpose of characterizing protein dynamics.\[^2\]

Figure 7 and Table 3 which characterize the shape of the distribution \( P(\Delta N_c, \Delta N_{cp}) \), illustrate the dramatic differences between polymeric and colloidal rearrangements during logarithmic relaxation. Polymeric rearrangements are significantly more correlated than those for colloids. For example, the correlation coefficient

\[
c = -\frac{\langle (\Delta N_c - \langle \Delta N_c \rangle)(\Delta N_{cp} - \langle \Delta N_{cp} \rangle) \rangle}{\sqrt{\langle (\Delta N_c - \langle \Delta N_c \rangle)^2 \rangle \langle (\Delta N_{cp} - \langle \Delta N_{cp} \rangle)^2 \rangle}},
\]

where the averages are taken over all rearrangements, is larger by a factor of 2.5 and the cross correlation \( \langle \Delta N_c \Delta N_{cp} \rangle \) is larger by a factor of 7.4 for polymers compared to colloids. The second moments of \( P(\Delta N_c, \Delta N_{cp}) \), \( \langle (\Delta N_c)^2 \rangle \) and \( \langle (\Delta N_{cp})^2 \rangle \), are also larger for polymers than colloids.

**Table 3** Statistical analysis of the data presented in Fig. 7. The top two rows are calculated by fitting to data in Fig. 4 in the preterminal regime \( (10^{6.5} \leq t \leq 10^7) \). The middle column shows data for colloidal rearrangements excluding “floaters”.

| Quantity | Colloids | Colloids (NF) | Polymers |
|----------|----------|---------------|----------|
| \( \partial \langle N_c \rangle / \partial \log_{10} t \) | 6.3 | 6.3 | 1.4 |
| \( \partial \langle N_{cp} \rangle / \partial \log_{10} t \) | 2.1 | 2.1 | 0.7 |
| \( \langle N^2_c \rangle \) | 9.1 | 2.2 | 23 |
| \( \langle N^2_{cp} \rangle \) | 0.41 | 0.32 | 3.2 |
| \( \langle N_c N_{cp} \rangle \) | 0.66 | 0.39 | 4.9 |
| \( c \) | 0.23 | 0.34 | 0.58 |

An interesting feature of \( P(\Delta N_c, \Delta N_{cp}) \) is that it is nonzero in quadrants II and IV (i.e. negative \( \Delta N_c, \Delta N_{cp} \)). Rearrangements occur in which the number of close-packed monomers decreases but the number of contacts increases overall, and vice versa. These are less likely for polymers than for colloids since covalent bonds impart greater cooperativity to rearrangements in polymers. \( P(\Delta N_c, \Delta N_{cp}) \) is reasonably well fit by a 2D Gaussian functional form

\[
P^*(\Delta N_c, \Delta N_{cp}) \propto e^{-(E(\Delta N_c)^2 + F \Delta N_c \Delta N_{cp} - G(\Delta N_{cp})^2)},
\]

where \( E \) is similar for polymers and colloids, \( F \) is larger for polymers, \( G \) is larger for colloids, and \(-F/(2EG)\) is larger for polymers. These results are consistent with our finding that \( c \) is larger for polymers than for colloids.

The fit \( P^*(\Delta N_c, \Delta N_{cp}) \) does, however, fail to capture several key features of rearrangements. In particular, \( P(\Delta N_c, \Delta N_{cp}) \) has a sharper peak at the origin and “fat” (wider than Gaussian) tails. The fat tails of \( P(\Delta N_c, \Delta N_{cp}) \)
are dominated by events where a monomer escapes from or rejoins the crystallite (for colloids), or a chain end becomes “floppy” (for polymers). These events tend to be associated with rearrangements with large $\Delta N_c$ and small $\Delta N_{cp}$ for colloids, and large $\Delta N_c$ and $\Delta N_{cp}$ for polymers (the difference being that covalent bonds impart a large degree of coupling between the exterior and close-packed interior of crystallites). While rare, these events may dominate large rearrangements in which many changes of contacts occur.

To quantify this effect, we analyze colloidal rearrangements with “floaters” excluded, i.e. where all particles possess at least one interparticle contact both before and after the rearrangement. Since monomers in polymers always have at least one contact, excluding floaters provides a more direct method to quantify the role of topology in controlling the rearrangements occurring during slow crystallite growth.  Figure 7(b) and the “Colloids (NF)” data in Table 3 present this analysis. The “no-floater” subset of colloidal rearrangements possesses significantly smaller fluctuations (in terms of $\langle \Delta N_c^2 \rangle$ and $\langle \Delta N_{cp}^2 \rangle$) and is more correlated (in terms of $\langle \Delta N_c \Delta N_{cp} \rangle$). However, no-floater colloidal rearrangements remain significantly less correlated than those for polymers. Thus we claim that the distributions $P(\Delta N_c, \Delta N_{cp})$ differ dramatically for polymers and colloids (i.e. are more correlated for polymers) precisely because their free energy landscapes are different, which in turn is a direct consequence of the presence or lack of covalent bonds.

The large width of the distribution $P(\Delta N_c, \Delta N_{cp})$ implies that the dynamics of crystallite growth in the pre-terminal relaxation regime are highly heterogeneous, especially for polymers. One source of dynamical heterogeneity, as suggested by Fig. 7, is surface effects. Rearrangements at the surfaces of crystallites (where monomers possess low $\eta$) are qualitatively different than those occurring within the close-packed cores. To illustrate the role of surface effects and covalent bonds, we now compare typical rearrangement events characteristic of those occurring in $(N = 100)$ polymeric and colloidal crystallites.

Visualization of typical rearrangements in polymeric and colloidal crystallites: Figure 8 shows a colloidal rearrangement with $\Delta N_c = 8, \Delta N_{cp} = 2$ ((a) and (b)) and a polymeric rearrangement with $\Delta N_c = 7, \Delta N_{cp} = 4$ ((c) and (d)). These are roughly equiprobable, with $\log_{10} P(\Delta N_c, \Delta N_{cp}) \approx -3.5$, and the ratio $\Delta N_{cp}/\Delta N_c \approx c$. (See Table 3) Before the colloidal rearrangement, the red monomer has only one contact; during the rearrangement, it settles into a groove on the surface of the crystallite and adds three new contacts. At the same time, the right hand side of the crystallite undergoes a large rearrangement, which improves its stacking order, and five other contacts and two other close-packed atoms are added elsewhere. It is likely that the initial “looseness” of the red monomer destabilizes the crystallite and gives rise to the soft mode that causes this large rearrangement.

For polymers, the picture is qualitatively similar, but is further complicated by the fact that the interior and exterior of crystallites are topologically connected. Large rearrangements are often initiated when a chain end is at the surface and relatively loose. Note that in Fig. 8(c) and (d) the color varies
Fig. 8 Visualizations of typical moderately-sized rearrangement events for polymeric and colloidal crystallites. Panels (a) and (b) show the colloidal crystallite before and after a colloidal rearrangement event with $\Delta N_c = 8$ and $\Delta N_{cp} = 2$ and (c) and (d) show the polymeric crystallite before and after a polymeric rearrangement event with $\Delta N_c = 7$ and $\Delta N_{cp} = 4$. The orange color shading in (c) and line in (d) show where new close-packed particles are added.

from red to green to blue as the monomer index increases from 1 to 100. Before the rearrangement, the chain end including monomer 100 is relatively loose (with only 3 contacts), and a pocket exists in the crystallite with above average free volume. During the rearrangement a segment of the polymer including this end executes a “flip” that collapses the pocket. The chain end monomer adds three contacts, and four other contacts and close-packed atoms are added elsewhere.

Covalent bonds suppress large rearrangements less when chain ends exist on the exterior of crystallites. In the rearrangement event depicted in Fig. 8(c) and (d), the path of the covalent backbone through the crystallite is not particularly tortuous—it proceeds in a relatively orderly fashion from upper-right to lower-left. Entropic factors such as “blocking” suppress the probability for chain ends to exist in the interior, otherwise large rearrangements would be even further suppressed.

In summary, despite qualitative similarities, polymer topology produces the large quantitative differences in slow crystallite growth and rearrangements illustrated above in Figs. 4-8 and Table 3. Even larger and rarer polymeric rearrangements than those depicted in Fig. 8 involve cooperative rearrangements of sub-chains that do not include chain ends. Such large-scale rearrangements occur within the interior of the crystallite; their initiation requires a large (negative) $\Delta N_c$ and $\Delta N_{cp}$, and hence they possess large activation energies. These are the slowest relaxation mechanisms, and it is likely that they control the approach to the ergodic limit in polymer crystallites.

4 Discussion and Conclusions

In this article, we compared the crystallization dynamics of single-chain polymers and colloids. The use of model systems with hard-core-like repulsive and short-range attractive interparticle potentials yielded contact-dominated crystallization and allowed us to characterize crystalline order via measures such as the number of contacts $N_c$, the number of close-packed particles $N_{cp}$, and the contact degree distribution $P(\eta)$. Our use of a model in which covalent and noncovalent bonds have the same equilibrium bond length yielded the same low energy structures for polymeric and colloidal systems, allowing us to isolate the role of chain topology on the dynamics of crystallite formation and growth.

Particular attention was paid to the effect of thermal quench rate. Slow thermal quench rates yield first-order like transitions to crystallites at $T = T_{\text{cryst}}$. The ratio of $T_{\text{cryst}}$ for polymers to that for colloids can be obtained roughly by counting degrees of freedom. Comparison of polymeric and colloidal crystals at equal values of $T/T_{\text{cryst}}$ showed they possess similar structure (i.e. $N_c$, $N_{cp}$, and $P(\eta)$), and thus occupy similar positions on their respective free energy landscapes, despite significantly different absolute $T$. Higher quench rates yielded rate-dependent effects and glassy relaxation from partially disordered to more ordered configurations. While the marked slowdown in dynamics at $T = T_{\text{cryst}}$ and consequent rate-dependent glassy behavior for crystal-forming systems possessing phase diagrams like Fig. 2(a) is understood in terms of a crossover to potential energy landscape dominated dynamics with decreasing temperature, the role of covalent backbones (and consequently, different energy landscapes) in producing the strongly differing nonequilibrium responses for polymers and colloids reported in this paper has not been pre-
Crystallites can rearrange in many different ways (e.g. with different changes $\Delta N_c$ and $\Delta N_{cp}$ in the number of contacts and close-packed monomers, respectively). By measuring the transition probability $P(\Delta N_c, \Delta N_{cp})$ in the regime where the degree of crystalline order exhibits slow logarithmic growth, we characterized how the rare collective rearrangement events which control the slow approach of crystallites to equilibrium are affected by polymer topology. Significant differences between $P(\Delta N_c, \Delta N_{cp})$ in polymeric and colloidal crystallite formation are attributable to the increased cooperativity of rearrangements required by the covalent backbone.

Strong finite size effects have been observed in both equilibrium and nonequilibrium polymer-collapse studies.\textsuperscript{2,11,25} Here we examined system size effects using measures of order such as $N_c$ and $N_{cp}$ that vary rapidly with the number of particles $N$ due to concomitant variation in the ratio of crystallite surface area to volume. This variation did not change any of the qualitative features reported above, and quantitative differences were as expected: dynamical slowdown of relaxation associated with restricted motion imposed by the covalent backbone strengthens with increasing $N$.

It is well known that bond-angle interactions play a significant role in controlling crystallization of most synthetic polymers. While this study considered flexible chains, it serves as a basis for future studies of more realistic models by elucidating the role polymer topology plays in controlling the glassy dynamics of crystallization. Our results may also be directly applicable to understanding the collapse behavior of flexible "colloidal polymers", which have recently been shown to self-assemble into tunable, compact nanostructures,\textsuperscript{25} as well as very flexible natural polymers such as single stranded DNA.\textsuperscript{26} Future work will examine how crystallization and packing are affected by semiflexibility, as well as effects of topology on the dynamics of equilibrium crystallites.

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