

## Slow dynamics, aging, and crystallization of multiarm star glasses

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Multiarm star polymers are model systems with tunable intermediate colloid to polymerlike character, exhibiting rich phase behavior, internal relaxations, and flow properties. An important puzzle for several years has been the lack of clear experimental proof of crystalline states despite strong theoretical predictions. We present unambiguous evidence via multispeckle dynamic light scattering (MSDLS) and small-angle neutron scattering (SANS) for such crystallization in a solvent of intermediate quality. An unexpected speed up of the short-time star diffusion observed in MSDLS was attributed by SANS to crystallization, via aging, of the multiarm star glass. This delayed glass to crystal transition establishes a pathway for star crystallization that might be generic in colloidal glasses.

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The interplay of thermodynamic equilibrium phases with metastable nonergodic states is one of the most intriguing and less well-understood phenomena in condensed-matter physics. In a variety of liquids the structural relaxation slows down dramatically upon reducing temperature or increasing concentration, while beyond the liquid-glass transition crystallization is suppressed by an intervening glassy state [1–3]. The latter is often aging as evidenced by intrinsic dynamics slowing down with waiting time [4,5]. Recent molecular-dynamics simulations in hard spheres suggest that spontaneous crystallization from an aging glass with no out-of-cage diffusive motion is possible [6]. Multiarm star polymers are established as a unique model system with tunable interactions spanning the regime between hard spheres and soft interpenetrable flexible polymers [7–9]. As such they attracted significant theoretical and experimental attention, in an effort to explore effects of interparticle interactions on a variety of phenomena from equilibrium phase behavior and nonergodic transitions to microscopic dynamics and macroscopic flow properties.

Star polymer solutions are expected to crystallize near their overlap concentration due to enhanced osmotic pressure [10]. Although a rich phase diagram containing a variety of thermodynamically stable crystal phases has been predicted by Monte Carlo simulations and theory [11,12] so far there is no unambiguous experimental evidence of any crystal formation of multiarm stars [8,13] except for some fragmental small-angle neutron scattering (SANS) data [14] and contrary to diblock copolymer micelles at rest [15,16] or after small shear [17]. Instead, at high concentrations nonergodic states were often encountered either increasing number density [18], similarly to hard spheres or temperature at intermediate-quality solvent [19] due to an increase in the effective volume fraction via thermal swelling of the polymer arms. Even for starlike micelles, whose interactions and

structure factor largely resemble those of stars, crystallization was only observed at intermediate functionalities [20]. Brownian dynamics simulations and mode coupling predictions provided some theoretical understanding of the observed arrested states [12] while recent simulations indicated a kinetic amorphous-to-crystal transition in multiarm stars in marginally good solvent [21]. Still the elusive character of star crystallization remained an open problem introducing debates on the validity of the theoretical predictions or the quality of samples and thus of a variety of experimental findings. The lack of experimental proof was often attributed to outer blob fluctuations and finite polydispersity effects that suppress ordering [8,13] while chain exchange and functionality variability in polymer micelles was considered to facilitate crystallization [22].

Here we present multispeckle dynamic light scattering (MSDLS) and SANS measurements of multiarm star glasses in an intermediate solvent, probing the time evolution of intrinsic dynamics and structure after a temperature jump from the liquid state. Such procedure revealed an unexpected pathway toward crystal formation via a slow aging of the initially frustrated glassy state providing unambiguous evidence for the long-awaited multiarm star crystallization. It further provided experimental proof for a glass to crystal transition in the absence of long-time out-of-cage motion diffusive motion. Such route to equilibrium may be proven generic in colloidal glasses, at least with repulsive interactions [6].

We used a regular protonated or deuterated 1,4-polybutadiene (PB) star [23] with  $f=122$  arms dissolved in an intermediate quality solvent (protonated tetradecane) [24]. The weight-average molar mass of the star arm was  $M_a=72\,000$  g/mol and its hydrodynamic radius and radius of gyration, measured by dynamic light scattering (DLS) and SANS at  $T=20$  °C, were  $R_H=45$  nm and  $R_g=38$  nm, respectively, while both increase with  $T$  toward their athermal values [25]. At a concentration of 6.3% by wt. [ $c/c^*=1.26$ , with  $c^*=3fM_a/(4N_A\pi R_H^3)$  calculated at 20 °C] the sample exhibits a liquid to glass transition at  $T\approx 20$  °C [25]. The

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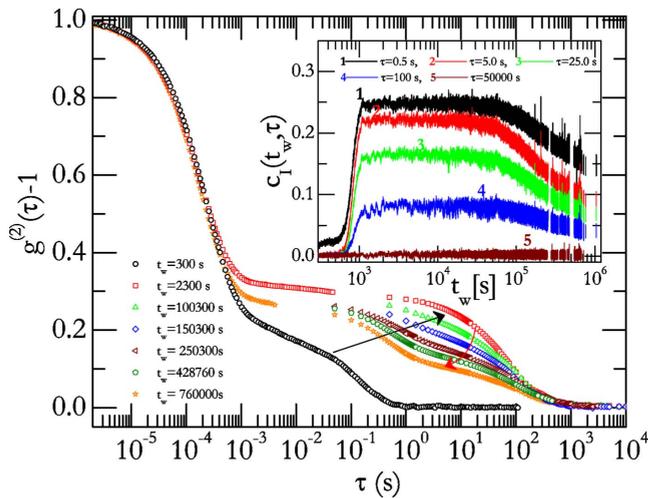


FIG. 1. (Color online) Time evolution of the correlation function in a 6.3% wt. ( $1.26c^*$ ) solution of multiarm stars in tetradecane after a temperature jump from  $T=15$  to  $25$  °C measured at  $q=0.024$  nm $^{-1}$  ( $\theta=90^\circ$ ). The arrows indicate the initial slowing down and subsequent speed up of the dynamics. Waiting times are indicated. Inset: corresponding degree of correlation for few sample times (1–5 as indicated) as a function of waiting time.

dilute  $R_g$  value gives a dimensionless packing fraction,  $\eta=(\pi/6)\rho\sigma^3=0.218$  (with  $\sigma=1.32R_g$  [7]) while the measured by SANS at  $c=6.3\%$ ,  $R_g=27.3$  nm, yields  $\eta=0.081$ . We follow aging of such glassy state as a function of waiting time,  $t_w$ , after a temperature jump from the liquid state at  $15$  °C to  $20^\circ$  (or  $25$  °C) by monitoring the slow dynamics and structure via MSDLS and SANS, respectively.

Dynamic light scattering was performed to calculate the time-autocorrelation function [2],  $g^{(2)}(q, \tau) = \langle I(q, t+\tau)I(q, t) \rangle / \langle I(t) \rangle^2$  of the scattered intensity,  $I(t)$ , at several wave vectors,  $q=[(4\pi n_2/\lambda_0)\sin(\theta/2)]$ , where  $n_2$  ( $=1.497$ ) the suspension refractive index,  $\lambda_0$  ( $=532$  nm) the laser wavelength and  $\theta$  the scattering angle. For the slow relaxation we utilized a home made MSDLS setup with a multipixel charge coupled device (CCD) camera detector ( $80 \times 300$  pixels at 2 or 20 frames/s). The fast part of  $g^{(2)}(q, \tau)$  was measured with a single-mode fiber and a photomultiplier tube (PMT) on a continuous slowly rotating sample averaging over a large number of speckles. After cutting off the decay due to sample rotation, the two parts were linked (Fig. 1). SANS measurements were performed at the Swiss spallation neutron source (SINQ). The raw data were corrected for detector efficiency, incoherent background scattering, and transmission and converted into absolute units using water as a standard.

We first present the dynamic light scattering data following a temperature jump from the liquid ( $15$  °C) to the glass ( $25$  °C). The degree of correlation between speckle patterns at time  $t_w$  and  $t_w+\tau$  given by  $c_I(t_w, \tau) = \langle I_p(t_w)I_p(t_w+\tau) \rangle_p / \langle I_p(t_w) \rangle_p \langle I_p(t_w+\tau) \rangle_p - 1$ , with  $I_p(t_w)$  the time dependent intensity of the  $p$ th pixel and  $\langle \dots \rangle_p$  the average over all CCD pixels, monitors temporal changes in intensity correlations [26]. Averages of  $c_I(t_w, \tau)$  over a short time window, with stationary dynamics, provide the two-time correlation function,  $g^{(2)}(t_w, \tau) - 1$ , representing the evo-

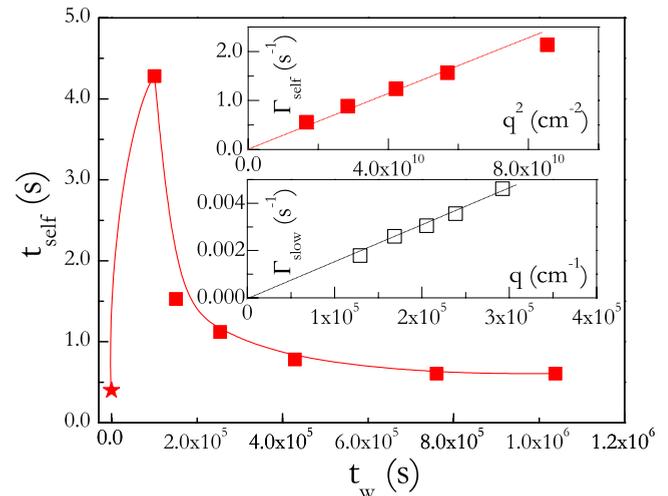


FIG. 2. (Color online) Relaxation time of the self-diffusion mode at  $\theta=90^\circ$  as a function of waiting time (solid). Inset:  $q$  dependence of the decay rates for the self-diffusion (solid) and ultraslow relaxation (open) process.

lution of aging dynamics (over longer times) with waiting time  $t_w$ . The time evolution of  $c_I(t_w, \tau)$  and  $g^{(2)}(t_w, \tau)$  immediately after jumping into the glassy state (at  $T=25$  °C) is shown in Fig. 1. For all delay times,  $\tau$ ,  $c_I(t_w, \tau)$  exhibits an initial fast increase reaching a first plateau at  $t_w \sim 10^3$  s resulting into a rapid slowing down of the slow relaxation mode in  $g^{(2)}(t_w, \tau)$  by about three decades, while the fast process, linked to the cooperative diffusion of the star polymer arms [18], is unaffected. Note that the sample at  $25$  °C exhibits a rheological solidlike behavior with no indication of terminal relaxation [25]. Yet, the existence of a slow relaxation process indicates the activated type of ultraslow dynamics present in a wide range of frustrated systems [5,27]. Although the existence of such aging, slow modes is expected in glassy materials, a surprising observation is revealed for waiting times longer than about  $10^5$  s: the degree of correlation starts to decrease toward a second steady state plateau leading to a speed up of the slow dynamics that eventually splits into two modes. Such unprecedented behavior signifies a path of this soft glass toward a steady state.

After  $\sim 10^5$  s the faster of the two slow processes speeds up whereas the slower one is stationary. The evaluation of the corresponding relaxation times is feasible via an inverse Laplace transform (ILT) assuming a superposition of single exponential decays,  $g^{(2)}(\tau) - 1 = \int L(\ln t) \exp(-\tau/t) d \ln t$ , common in polymeric systems. The angular dependence of the decay rate,  $\Gamma(=1/t)$  [28], for these two modes is shown in the inset of Fig. 2. The intermediate mode with  $\Gamma_{self} \propto q^2$  has been identified with the star short-time self-diffusion which is tractable by light scattering at low  $qR$  due to finite star polydispersity giving rise to incoherent scattering [2,8,18]. The slow one however reveals  $\Gamma_{slow} \propto q$  indicative of non-diffusive ultraslow dynamics commonly observed in a large variety of frustrated soft matter systems and attributed to the relaxation of internal stresses [5]. Note that the larger length scale probed ( $qR_g=0.35$  at the lowest  $q$ ) is  $\sim 3$  particle radii corresponding to distances of about one to two cages. The lack of a nonergodic plateau proves that concentration fluctu-

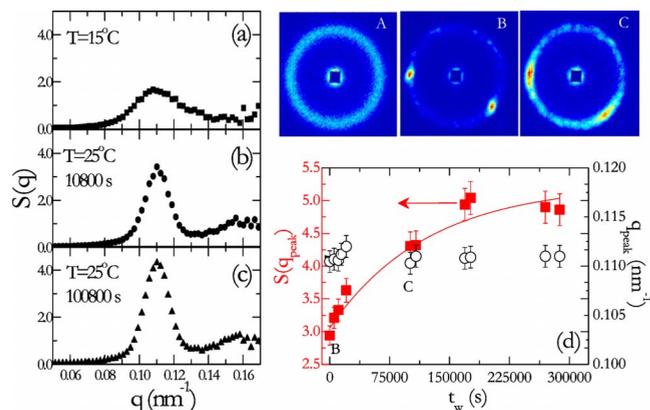


FIG. 3. (Color online) Time evolution of SANS data from a 6.3% multiarm star solution in tetradecane at  $T=25$  °C after temperature jump from 15 °C. On the left: Structure factor taken at (a) 15 °C and [(b) and (c)] at 25 °C at different waiting times. The corresponding 2D SANS images are shown at the top. Clear evidence of Bragg reflections is seen after 3 h. (d) Amplitude (solid square) and position (open circle) of the structure factor peak.

tuations relax totally over this length scale via the observed three modes; hence there is no long-time out-of-cage diffusion over the distance of a couple of cages. Figure 2 depicts the time evolution of the self-diffusion with the initial slowing down after temperature jump into the glass regime followed by a gradual speed up, leading to a final steady state at long times.

The speed up of slow dynamics as the multiarm star glass ages brings forward the generic question of the underlying mechanism that drives aging in colloidal glasses and the related structural changes. The picture of an energy landscape evolving with time toward metastable states with deeper local minima where it is trapped for longer times [29] gives rise to progressively slower dynamics, in accordance with experimental observations in various glassy systems. To the contrary, the speed up observed here can only be rationalized with the conjecture that the star glass eventually evolves toward a crystal at long times. In this case ordering leads on average to locally enhanced free volume resulting in faster particle dynamics. To test such hypothesis, we performed SANS measurements following exactly the same experimental protocol.

In Fig. 3 we show the time evolution of the structure factor,  $S(q)$ , and the corresponding two-dimensional (2D) SANS images for a 6.3% ( $c/c^*=1.26$ ) sample at  $T=25$  °C after a fast temperature jump from the liquid state at 15 °C.  $S(q)$  was calculated from the radially averaged SANS intensity of the concentrated deuterated star after subtraction of the incoherent scattering and then normalized by the form factor. The latter was measured in a concentrated solution of protonated star with 0.1% deuterated star (total  $c=6.3\%$ ) in protonated tetradecane. In agreement with DLS (Fig. 1) and rheology [25] the sample at  $T=15$  °C is liquid as suggested from the radially symmetric 2D SANS (image A) and  $S(q_{peak}) < 2$ . After the temperature is increased to  $T=25$  °C the amorphous ring of the 2D SANS image slowly disappears, while two distinct Bragg spots are formed in few thousand seconds (image B, Fig. 3) with  $S(q_{peak}) \sim 3$  and higher

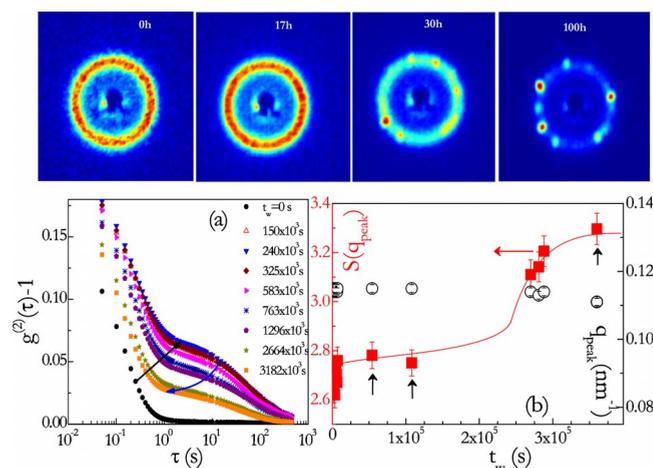


FIG. 4. (Color online) Time evolution of the dynamics and structure in a 6.3% multiarm star solution after a temperature jump from  $T=15$  °C to  $T=20$  °C: (a) slow part of the correlation function at various waiting times as indicated and (b) Amplitude (solid square) and position (open circle) of the structure factor peak along with 2D images at  $t_w=0, 17, 30,$  and 100 h. Arrows denote the times when 2D SANS data were collected.

order peaks appearing. Subsequently, a slow evolution with time is observed with the first-neighbor ring in the 2D Bragg image gaining in intensity and decreasing in radial width (image C) suggestive of bigger and better crystallites. The main peak increases toward a steady state value of  $S(q_{peak}) \sim 5$  after almost 50 h [Fig. 3(d)]. These high  $S(q_{peak})$  values exceed significantly 2.85, the empirical Hansen-Verlet criterion [30] for crystallization confirmed by theory and simulations for multiarm stars [7]. Moreover,  $q_{peak}$  is virtually unaffected by the glass-crystal transition since the average distance between first neighbors depends only on number concentration.

The Bragg spots in the 2D image and the high  $S(q_{peak})$  values provide unambiguous proof of crystallization through slow aging of the initial glassy state of multiarm stars. Note that at the final steady state  $S(q)$  data at high  $q$  (not shown) cannot clearly distinguish between an fcc and bcc structure. The asymmetric Bragg spots (image B, Fig. 3) which may be attributed to incomplete averaging over few randomly oriented crystallites become stronger (image C, Fig. 3) while the azimuthal width, which is a measure for orientation distribution, broadens.

We further investigated the behavior closer to the liquid-solid transition [25]. MSDLS and SANS experiments at  $T=20$  °C, after jumping from the liquid (15 °C) (Fig. 4), reveal qualitatively the same mechanism. The slow modes in  $g^{(2)}(t_w, \tau)$  initially grow in strength and become slower but after few thousand seconds they start speeding-up and reach a steady state in several days [Fig. 4(a) and 4(b)]. Compared to 25 °C, SANS data reveal a much longer-lived glassy state before crystallization commences, with the first weak crystalline spots appearing after a day and the peak of  $S(q)$  exceeding three after more than two days (Fig. 4) suggesting a weaker driving force closer to the transition. However whether such behavior persists at even higher temperatures (well into the glass regime) or whether the system is trapped

in a stronger glassy state remains an unresolved question. Note that earlier preliminary measurements on a similar star (same  $f$  but smaller  $M_a=7000$ ) showed symmetric Bragg peaks when concentrated athermal solutions were presheared [14] confirming the shear induced crystallization but not addressing the connection between aging and crystallization close but above vitrification. Moreover here a temperature drop to 15 °C leads to crystal remelting providing an efficient way to rehomogenize the system avoiding shear.

Summarizing, we have presented clear experimental evidence for the crystallization of multiarm stars via a well-controlled pathway in an intermediate quality solvent where the effective volume fraction is tuned by temperature. Crystallization emerges through aging of a glassy state in which the system is trapped immediately after a temperature jump from a liquid state. During crystallization, the slow relaxation of  $g^{(2)}(t_w, \tau)$  related to star short-time, in cage, diffusion progressively speeds up due to creation, locally, of larger free volume via ordering of the stars. Moreover, long-time diffusion over distances of one to few cages is absent and replaced by an ultraslow nondiffusive relaxation typical

in soft matter glasses. Hence, we have identified experimentally a novel pathway to star crystallization through an intriguing aging of the glass in the absence of simple long-time diffusion, reminiscent of recent computer simulations in hard spheres [6] that might be generic in glasses with repulsive interactions and possibly even broader [31]. In fact, the softness of the particles here (arms fluctuations) maybe experimentally beneficial in observing the glass-to-crystal transition faster compared to the hard sphere case proposed in [6]. Crystallization is slower closer to the liquid-solid transition, revealing a longer-lived glassy state. The detailed effects of concentration proximity to melting temperature and shear on the kinetic pathway toward crystallization will be the subject of future work.

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