Tailoring the Flow of Soft Glasses by Soft Additives

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We examine the vitrification and melting of asymmetric star polymer mixtures by combining rheological measurements with mode coupling theory. We identify two types of glassy states, a single glass, in which the small component is fluid in the glassy matrix of the big one, and a double glass, in which both components are vitrified. Addition of small-star polymers leads to melting of both glasses, and the melting curve has a nonmonotonic dependence on the star-star size ratio. The phenomenon opens new ways for externally steering the rheological behavior of soft matter systems.

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The design of materials with well-defined rheological properties and the ability to alter these at will, by tuning suitable control parameters of the system, are issues of central importance in today’s soft matter research. Experimental findings, accumulating at a fast pace, call for the identification and profound understanding of the several underlying physical mechanisms that control the ability of soft materials to support stresses or flow under shear [1]. In several situations, e.g., in coating or processing applications, it is necessary to dramatically alter the viscoelastic properties of a material. One possibility to do so in a controlled way is to exploit the phenomenon of dynamical arrest. Indeed, close to a liquid-glass transition, a small variation of external parameters produces a spectacular change in the elastic properties of the material without significantly affecting its structure [2].

Star polymers have emerged as an ideal model system for exploring the flow behavior of soft matter and elucidating its molecular origin. They consist of f polymer chains covalently anchored onto a common center [3]. Star-polymer solutions are chemically simple, well-characterized, and physically tunable in their softness, building thereby natural bridges between hard colloids and polymers. This property stems from the particular form of the effective, entropic interaction between star-polymer centers [4,5], which has a logarithmic (Yukawa) form at small (large) separations. Technologically, star polymers are important in several applications, such as their use as viscosity modifiers in the oil industry [3] or their novel applications as drug-delivery agents [6,7].

In this work, we show how one can gain control over the rheological properties of soft, repulsive, glassy materials via the addition of a second, soft, repulsive component, which is chemically identical to the first but smaller in size. We consider a star-polymer glass perturbed by smaller star-polymer additives. We observe melting of the big-star glass, induced by the small stars, and an unexpected nonmonotonic dependence of the critical amount of additives, needed to melt the glass, on the big-small star size ratio. We also perform the corresponding calculations of the melting line, within the binary mode coupling theory (MCT) framework [8,9]. The theoretical melting line is in agreement with the experimental one, reproducing the qualitative trends of the latter. We demonstrate that the nonmonotonic behavior arises from two different mechanisms by which the presence of the additive significantly affects the rheological properties, depending on the size ratios between the components. The former rests on the fluidity of the smaller component in the single glass formed by the larger component. The latter stems from the mutual soft repulsions in the double glass, in which both components are vitrified. The melting of such a double glass represents a novel physical process, in which a glassy component is liquefied through the addition of a second glassy component.

Binary mixtures of big and small (1,4-polybutadiene) stars were prepared in toluene. Three different types of big stars were employed, having an average functionality \( f_1 \) \( \equiv 270 \) arms and arm molecular weight \( M_a \) ranging from 18 000 to 42 000 g/mol [10]. Soft glasses were obtained at concentration \( c_1/c_2^* \equiv 1.4 \), where \( c_2^* \) denotes the big-star overlap concentration. Additional measurements were also performed with big stars of functionality \( f_1 = 128 \) with arm molecular weight of about 80 000 g/mol, which are very similar to the 270 stars [11]. We express the mixture composition by the values \( \rho_1 \sigma_i^2 \) of the big and \( \rho_2 \sigma_i^2 \) of the small stars, where \( \rho_i, i = 1, 2 \) are the respective number densities and \( \sigma_i \) are the corona diameters of the big stars.
appearing in the effective interactions employed in the theory, coinciding with the stars’ hydrodynamic radii \( R_{h,i}, i = 1, 2 \). Small stars with three different functionalities \( f_i = 16, 32, \) and 64 and molecular weights \( M_p \) between 1200 and 80000 g/mol [12–14] were synthesized as well. Size ratios \( q = R_{h,2}/R_{h,1} = \sigma_2/\sigma_1 \) varied from 0.15 to 1. The mixture preparation protocol consisted of creating the big-star glass at fixed number density \( \rho_1 \sigma_1^3 = 0.345 \) \((c_1/c_1^* = 1.4)\) and then adding small stars with certain \( q \) at a desired density \( \rho_2 \), under conditions of very gentle and prolonged stirring. In this procedure, the glass was broken and the mixture was left to “equilibrate” again. For the \( f_i = 128 \) sample, the fixed density was \( \rho_1 \sigma_1^3 = 0.412 \). Dynamical rheological measurements (time, strain, and frequency sweeps) were carried out in order to identify the state of the particular samples (solid or liquid behavior). A strain-controlled rheometer was utilized in the cone-and-plate geometry (25 mm diameter, 0.04 rad cone angle), and dynamic frequency sweep tests were conducted in the range 100–0.1 rad/s at 20 °C in the linear viscoelastic regime.

The experiments carried out provide evidence of U-shaped melting curves in the \((q, \rho_2)\) plane as well as quantitative distinctions of two types of glasses depending on the value of \( q \). The glassy samples are characterized by the typical virtually frequency-independent elastic moduli \( G' \) (350 Pa < \( G' < 800 \) Pa) and respective weakly frequency dependent viscous moduli \( G'' \) that exhibit a broad minimum (20 Pa < \( G''_{\text{min}} < 55 \) Pa) [15]. For a small concentration of small stars, the system exhibits moduli \( G' > G'' \) and \( G' \sim \omega^0 \), characteristic of solid, glasslike behavior [15–17]. As the density of the added small star increases, there is a dramatic change in the mixture’s viscoelastic response. The glass melts, and a fluid results, whose modulus, and a fluid results, whose modulus are weaker by orders of magnitude. A compilation of rheological results obtained from the available samples of different \( q \) and \( \rho_2 \) is presented in Fig. 1 for both studied functionalities of the large stars. In order to have a clear representation of all results in one plot, only the data closest to the glass-liquid boundaries are shown. The results suggest that a U-shaped melting line separates the fluid (above) from the glass (below) states. This trend is general, since it is independent of the big stars used. Our theoretical analysis is based on a coarse-grained star description employing effective interactions [5] in binary star mixtures [18] with functionalities \( f_i \) and corona diameters \( \sigma_i, i = 1, 2 \), combined with MCT [8,9]. In the pure star solution, MCT predicts a glass line at large \( f \) above an \( f \)-dependent density [19], in agreement with experiment [2]. The equilibrium structure factors \( S_{ij}(k), k = 1, 2 \), were calculated by solving the two-component Ornstein-Zernike equation [20] within the Rogers-Young closure [21]. The dynamics was calculated using two-component MCT [22,23].

Upon addition of the smaller stars, the partial static structure factor \( S_{11}(k) \) of the large ones shows a loss of structure, a phenomenon caused by the depletion-induced softening of the repulsions between the big stars. At the same time, the small-stars partial structure factor \( S_{22}(k) \) gradually develops growing peaks. These structural changes result into melting of the glass at a \( q \)- and \( f_2 \)-dependent density \( \rho_m^{\text{melt}} \). Our theoretical results are summarized in Fig. 2. In agreement with experimental results, a characteristic U shape is found for the melting curves at all studied \( f_2 \). Above \( q = 0.4 \) for \( f_2 = 64 \), and \( q = 0.45 \) for \( f_2 = 16 \) and 32, no melting is found for any density of the small stars.

The U shape of the melting line points to the existence of two distinct microscopic melting mechanisms. For a very small size of the additives, a standard depletion mechanism takes place. The osmotic pressure from the mobile, small stars, which are free to diffuse in the matrix formed by the big ones, leads to a reduction of the repulsive interactions between the latter. As a consequence, the cages that stabilize the glass are weakened, eventually breaking at a sufficiently high small-star concentration, at which the system melts. Since depletion is stronger at fixed \( \rho_2 \) as \( q \) grows, the melting curve has, in this regime, a negative slope in the \((q, \rho_2)\) plane, generating the left arm of the U-shaped line. However, as \( q \) further increases, the smaller stars become themselves slower and they begin to actively participate in the glass formation. At low additives concentration, the latter become trapped in the voids left out of the glassy matrix. Hence, two competing mechanisms are at work: As before, the structure of the big stars is weakened by the addition of the small ones, but, at the same time, the second component becomes increasingly glassy. The onset of this mechanism brings about a reversal of the slope of the melting curve, since now the tendency of the small stars...
to soften the repulsion between the big ones is counter-driven by their own opposing tendency to jam. As \( \rho_2 \) grows at fixed \( q \), the small-star jamming cannot persist indefinitely, since the direct repulsions between the additives prevent them from occupying the same region of free space. As a result, melting of the glass takes place. We can distinguish between two different glassy states under the U curve, one in which only the big stars are jammed (low \( q \)) and one in which both components are arrested (large \( q \)). We call the former a single-glass state and the latter a double-glass state.

The above interpretation is supported, first, by a comparison with the results obtained if a one-component MCT treatment is adopted, in which the smaller stars are assumed to form an ergodic fluid (dotted lines in Fig. 2). The two approaches yield very similar results at small size ratios, whereas the discrepancy becomes larger at higher \( q \)’s, signaling the tendency of the small component to arrest. The deviation between the two approaches can also be understood in terms of the scaling of the short-time mobilities with size ratio [24]: As \( q \rightarrow 1 \), the timescale separation between the two species disappears.

Further, we have calculated the elastic modulus \( G’ \) following Ref. [25]. In the inset in Fig. 3, we show the theoretical results for \( G’ \), demonstrating that, for \( q \lesssim 0.3 \), \( G’ \) has a maximum at \( \rho_2 = 0 \), whereas for the larger size ratio, \( q = 0.4 \), it has a minimum there. At small \( q \), the additives lower \( G’ \) through the softening of the big cages, whereas at high \( q \) they lead to stiffening of the glass through the fact that they are themselves driven to dynamical arrest. In Fig. 3, theoretical and experimental results for the normalized modulus \( G’/G_0’ \) are shown, where \( G_0 \approx 500 \text{ Pa} \) stands for the average value of the elastic modulus of the big-star glass, without any additives. Experimental results display the same trends predicted theoretically. For small \( q \), experimental values are much lower than the theoretical ones, because MCT is not capable of taking into account the vast discrepancy in the mobilities of the two species in highly asymmetric mixtures. However, at larger \( q \), in a full binary regime where the theory works best, the agreement between theory and experiments becomes almost quantitative.

Additional evidence for the fluidity of the small stars at low \( q \) values and their jammed nature at high ones is offered by the calculated nonergodicity factor \( f_{12}(k) \), shown in Fig. 4. Whereas the big-star nonergodicity factor \( f_{11}(k) \) is rather insensitive to \( q \), and remains roughly the same in all glassy states, \( f_{22}(k) \) shows a dramatic change. For \( q \lesssim 0.2 \), \( f_{22}(k) \) is very small and its nonzero values are confined to a very narrow, small \( k \) domain. Such nonergodicity factors are fully consistent with a mobile small component [26–28]. At high \( q \) values, \( f_{22}(k) \) has the typical range of a fully arrested system.

The phenomenon of glass melting through polymer addition has been observed in hard-colloid–polymer (CP) mixtures [29,30]. The physics and implications of this are, however, in our case very different. Whereas in the CP case the solid melts due to the induction of short-range

\[ \text{FIG. 2 (color online).} \text{ Theoretical kinetic phase diagram of binary star mixtures, calculated using MCT. The large-star functionality and concentration are fixed at the values } f_1 = 270 \text{ and } \rho_1 \sigma_1^3 = 0.345. \text{ The diagram is shown for three different functionalities } f_2 \text{ of the small stars. Circles: } f_2 = 16; \text{ squares: } f_2 = 32; \text{ triangles: } f_2 = 64. \text{ The lines going through the calculated points are guides to the eye. The cartoons display local arrangements in a single big-star glass with mobile small stars (left) and in a double glass in which there is mutual caging of both components (right).} \]

\[ \text{FIG. 3 (color online).} \text{ Plot of the ratio } G'/G_0' \text{, where } G_0' \text{ is the modulus of the system without additives, against size ratio } q \text{ close to melting. Theory refers to the case } f_2 = 32, \text{ while experiments refer to a compilation of several measured elastic moduli of star-star mixtures, obtained with different big and small stars at various concentrations of the additives. Inset: Dependence of the elastic modulus } G' \text{ of the glass on } \rho_2 \text{ (} f_2 = 32). \]
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