Polymer-Mediated Melting in Ultrasoft Colloidal Gels

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Star polymers with a high number of arms, $f = 263$, become kinetically trapped when dispersed in an athermal solvent at concentrations above the overlapping one, forming physical gels. We show that the addition of linear chains at different concentrations and molecular weights reduces the modulus of the gel, eventually melting it. We explain this linear polymer-induced gel-liquid transition in terms of effective interactions and star depletion. In the limit of very high linear-chain molecular weight a "reentrant gelation" is detected and attributed to bridging flocculation, analogous to that observed in colloidal dispersions.

One of the most intriguing features of colloidal dispersions is the wide range of rheological behavior they exhibit, from liquidlike to solidlike, and which depends primarily on their volume fraction [1–5]. This behavior is well established for hard spheres, which have received a great deal of attention; on the other hand, for soft spheres, such as hard colloids with grafted polymeric layers, it is intrinsically related to the changing thickness of the layer and thus to the strength and range of the repulsive interactions [6]. Star polymers with high functionality have emerged as a novel class of ultrasoft colloidal particles, characterized by wide ranging interactions with Yukawa-type repulsions at long distances and logarithmic repulsions at short ones [7,8]. At high volume fractions, achieved via manipulation of their effective thickness in conditions of varying solvent quality, these systems exhibit a liquid-solid transition, which is of kinetic, rather than thermodynamic, origin [9–11]. This type of dynamic arrest is described as glasslike gelation, bearing many similarities with both colloidal glass formation (crowding of single particles) and colloidal gelation (formation of clusters) [11], and represents a manifestation of jammed colloidal particles [12]. The great challenge with such transitions is how to achieve molecular control by tuning the dynamic response. This will have a significant scientific and technological impact as it will open the route for the rational design of soft materials with desired properties in a variety of situations. Mixtures of star polymers with linear polymers are an obvious choice (as many soft matter systems occur as mixtures), which, however, has been overlooked so far.

In this Letter, we demonstrate the dramatic and unexpected effects of the addition of linear chains to a star polymer gel. We show that the added polymer reduces the modulus of the gel and in the limit of high polymer molecular weight or concentration, the gel melts. Within the liquified region, the reduced star viscosity drops upon further addition of linear polymer. The effective star-linear polymer interactions are shown to be responsible for the observed counterintuitive phenomena, via a depletionlike mechanism which explains the gel-liquid transition. Eventually, for very high molecular weights a reentrant gelation is observed and attributed to bridging flocculation induced by the long polymer chains.

We used model 1,4-polybutadiene starlike entities that are virtually identical to ideal stars [11,13] with $f = 263$ arms and arm molecular weight 42 300 g/mol, (hydrodynamic radius $R_H^{st} = 63$ nm, gyration radius $R_g^{st} = 54$ nm), coded as LS6, synthesized via hydrosilylation chemistry [14]. At a concentration of 2.5% weight (wt) in the athermal solvent toluene (the star overlap concentration being $c^* = 1.8\%$), a gel is formed, characterized by nearly frequency-independent dynamic storage (G') and loss ($G'' < G'$) moduli over a wide frequency range. We also employed linear 1,4-polybutadiene chains of varying molecular weights M (1000 to 1 200 000 g/mol), and corresponding radii of gyration R_g^{lin} (from 1.1 to 59.8 nm), some obtained from Polymer Source, Canada. Several samples were prepared in toluene, all having a constant star concentration 2.5% (size polydispersity $<4\%$) and different linear polymer molecular weight and concentration, in order to span the "phase space" of the formed mixture. The main experimental tool was shear rheometry (Rheometric Scientific ARES 100 FRTN1 in the 25 mm diam parallel plate geometry, under solvent trap conditions to eliminate evaporation), for the characterization of the kinetic phase state of the samples. Some selective small angle neutron scattering (SANS) measurements were also carried out at the KWS II, Forschungszentrum Jülich, using a neutron wavelength of 0.63 nm and accessing the wave vector range $0.03 \text{ nm}^{-1} < Q < 0.3 \text{ nm}^{-1}$, in order to assess the star structure factor in a deuterated linear polymer/toluene environment in which only the stars are visible.

Measurements of the frequency-dependent linear viscoelastic moduli at $10\,°C$ for various star samples with added linear polymer of fixed molecular weight and varying concentration, revealed a remarkable weakening of the gel; this was manifested as a decrease of the moduli (in particular G') upon adding the linear polymer, and eventually the transition to liquid ($G' \sim \omega^2 < G'' \sim \omega$) above a certain linear polymer concentration (see Fig. 1). A similar effect of added linear polymer was observed when its concentration was kept constant and the chain length varied; as seen in the inset of Fig. 1, increasing the polymer molecular weight decreases the plateau modulus G_p' of the gel [$G_p' = G'(\omega \to \infty)$] or the reduced viscosity (over that of the linear polymer solution in toluene) of the induced liquid. An intriguing finding is that both the plateau moduli of the gels and the reduced zero-shear viscosities of the liquids for all linear polymer concentrations and molecular weights collapse onto master curves when plotted against the reduced linear polymer concentration c_{lin}/c_{lin}^*, where $c_{lin}^* = 3M/[4\pi N_A (R_H^{lin})^3]$, with the Avogadro constant N_A and the hydrodynamic radius R_H^{lin}. This is seen in Fig. 1 for linear polymer molecular weights below $360\,000\,g/mol$. The figure is universal as it demonstrates that the added linear polymer weakens the star gel and eventually melts it, whereas it further thins the induced liquid. It should be noted that the scaling shown in Fig. 1 does *not* hold for chain molecular weights $M > 360\,000\,g/mol$ ($R_g^{lin} > 31\,nm$), where a bridging flocculation mechanism apparently sets in, and reentrant gelation takes place (see Fig. 2). This "threshold" value of R_g^{lin} can be understood as follows: as will be shown below, the stars can be rendered as spheres of

diameter $\sigma = 64\,nm$ and number density $\rho_1 = 0.32\,\sigma^{-3}$ for the samples at hand. This yields an average star-star separation $a = \rho_1^{-1/3} = 93\,nm$ and hence the spaces filled with their outermost blobs have typical extent $\delta \equiv a - \sigma = 29\,nm$. For $R_g^{lin} < \delta$, the chains can be thus accommodated inside these spaces and behave as individual coils. For $R_g^{lin} > \delta$, a network forms instead.

The gel-liquid transition is well defined at $c_{lin}/c_{lin}^* = 0.088$. A compilation of the results from the dynamic rheological measurements is presented in the kinetic phase diagram of Fig. 2. It can be seen that for low molecular weights the mixture remains a gel for linear concentration as high as 5.5%. Increasing the molecular weight and/or concentration yields gel melting up to a molecular weight of $360\,000\,g/mol$, above which the reentrant gelation phenomenon is observed. In this regime, we have $c_{lin} > c_{lin}^*$ for most samples. Thus, the unexpected findings here relate to the gel-liquid transition with increasing molecular weight or concentration and the liquid-gel transition in the very high molecular weight limit. Similar effects were found in a recent study of the "sticky hard-sphere" system, modeling mixtures of hard colloids with linear polymers [15].

To account theoretically for these phenomena, we applied an approach based on effective interactions between the components of the mixture [16], demonstrating that the addition of the chains causes a drastic decrease of the peak of the star-star structure factor, with the effect becoming stronger as the chain size increases. We selected the centers of the stars (species 1) and the centers of mass of the linear polymer chains (species 2) as our effective coordinates. The effective interaction between two stars with their centers held at separation r, $v_{11}(r)$, has been already derived theoretically, and it has a logarithmic-Yukawa form [7]. Comparisons with SANS data from the pure $f = 263$-star solutions have established that with the
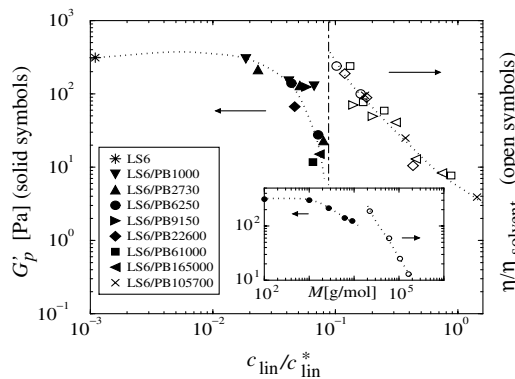

FIG. 1.   Plateau moduli G_p' of the gels (solid symbols) and reduced zero-shear viscosities of the liquids (open symbols) for various star-linear mixtures at constant star concentration (2.5%) and different linear polymer concentration and/or molecular weight (below $360\,000\,g/mol$), against the reduced concentration of the linear polymer, c_{lin}/c_{lin}^*. Lines are drawn to guide the eye. The vertical line denotes the gel-liquid transition. Inset: linear polymer molecular weight dependence of G_p' (solid symbols) and reduced zero-shear viscosity (open symbols) of star-linear mixtures at constant star (2.5%) and linear polymer (1.5%) concentrations. The vertical axes have the same labels as those of the main plot.
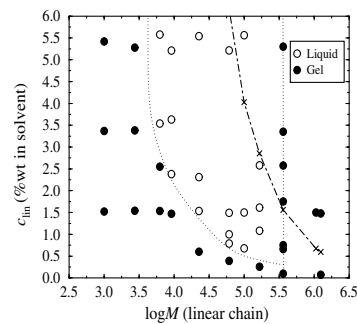

FIG. 2.   Kinetic phase diagram of star-linear polymer mixtures in toluene, in terms of linear polymer concentration against the respective molecular weight. Star concentration is 2.5 wt %. Open circles denote liquid and closed symbols denote gel. The vertical line denotes the onset of the reentrant gelation region and the curved dotted line is a guide to the eye, separating the liquid from the gel region. The $\times$ symbols mark the linear chain overlap concentrations c_{lin}^*. For $M < 100\,000$, c_{lin}^* lies above 6% (not seen in the figure).

choice $\sigma = 64$ nm $\cong 1.2 R_g^{\text{st}}$ [17], the theoretical structure factor obtained by using the interaction of Ref. [7] is very realistic [11]. The chain-chain interaction, $v_{22}(r)$, has a Gaussian form [18]: $v_{22}(r) = k_B T \varepsilon \exp[-(r/\tau)^2]$, where $\varepsilon = 1.87$ and $\tau = 1.13 R_g^{\text{lin}}$. The interactions $v_{11}(r)$ and $v_{22}(r)$ above define the chain/star size ratio $q = \tau/\sigma$.

For the cross interaction $v_{12}(r)$ between the stars centers and the linear polymer center of mass, we model the dense star as a sphere with diameter $d = \sigma(1 + 2/\sqrt{f})$, the additional term $2/\sqrt{f}$ taking into account the outermost blobs of the star [7,19]. We envision the chains as spheres of radius R_g^{lin} and make the physical assumption that, as the stars have a high functionality, the centers of mass of the chains can barely penetrate into the dense region of the latter. This implies a steep star-chain interaction for separations smaller than $\xi = d/2 + R_g^{\text{lin}}$. Were the stars hard, then a hard-sphere interaction of length scale ξ would be an appropriate modeling, as has been demonstrated in various studies of colloid-polymer mixtures [20]. However, as we are dealing with "soft colloids," we postulate a cross interaction that is somewhat softer and reads as $v_{12}(r) = \alpha k_B T(r/\xi)^{-12}$. The prefactor $\alpha \gtrsim 1$ can be estimated by considering the star–linear-chain interaction at separation $r = \xi$. There, the linear chain is interacting with loose arms from the star that are to be found in the region between $d/2 = 35$ nm and its hydrodynamic radius $R_H^{\text{st}} = 63$ nm. As the center of mass of the linear chain does not, in general, coincide with the center of mass of any of the loose chains, we expect the typical interaction energy at separation $r = \xi$ to be somewhat smaller than the value $\varepsilon = 1.87 k_B T$ mentioned above and depending on the size ratio q. To simplify the discussion and explore the trends, we have chosen in what follows the value $\alpha = 1.3$. The exponent -12 was also chosen arbitrarily. We have also modified both the exponent and the α value, finding that the results are qualitatively insensitive to such changes.

The weight fractions of stars and chains were converted into the dimensionless densities $\rho_1 \sigma^3$ and $\rho_2 \tau^3$, using the relation $\rho_i = \phi_i N_A \varrho_i / M_i$, $(i = 1, 2)$, where ϕ_i is the volume fraction, ϱ_i the mass density, and M_i the molecular weight of the ith component of the mixture. We obtain thus the star density $\rho_1 \sigma^3 = 0.32$, very close to the phase boundary of thermodynamic freezing into a fcc lattice [21]. This transition, however, is hindered by the jamming of the stars and a gel occurs instead.

We solved the two-component hypernetted chain (HNC) closure to calculate the partial structure factors of the mixture. Selected results are shown in Fig. 3, in which values of $\rho_2 \tau^3$ corresponding to the ones used in the experiments were employed. For the pure star system, the structure factor $S_{11}(Q)$ is seen to have a peak value of about 3.05, exceeding the Hansen-Verlet [22] freezing threshold of 2.85, and pointing thus to a metastable liquid. Upon addition of linear chains, a drastic decrease of this peak value is seen, accompanied by an increase of the $S_{11}(Q \rightarrow 0)$ value. The maximum of $S_{11}(Q)$ is brought
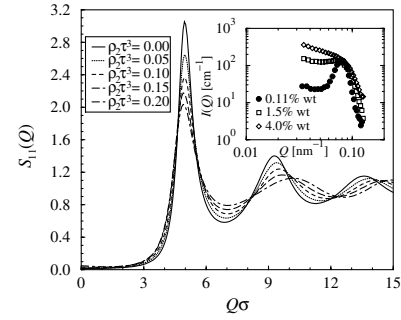

FIG. 3. The structure factor $S_{11}(Q)$ of the stars at star density $\rho_1 \sigma^3 = 0.35$ for various concentrations $\rho_2 \tau^3$ of added chains, and for size ratio $q = 0.30$. Inset: star-star SANS scattering intensities from a star-chain mixture at the same size ratio, at star weight fraction $c_{\text{star}} = 2.5$ wt % and for different chain concentrations c_{lin}, as indicated in the plot. Shown is only the Q range around the first maximum of $I(Q)$, which falls into the largest detector distance of 20 m.

below the Hansen-Verlet threshold. The loss of star-star correlations is more pronounced at larger size ratios. This feature, caused by depletion, is in agreement with the experimental finding that the melting of the gel is achieved at lower c_{lin} as the chain molecular weight grows, see Fig. 1 (inset) and Fig. 2.

The theoretical predictions were experimentally confirmed by performing SANS measurements with selected mixtures. The inset of Fig. 3 demonstrates the strong weakening of the pronounced peak of the star scattering intensity upon increasing c_{lin}. The virtual elimination of the peak at $c_{\text{lin}} = 4\%$ is caused by multiplying the form factor with a structure factor whose maximum is not sharp enough [23]. As we are dealing with stars at fixed concentration, their form factor is only minimally affected by the addition of chains that causes a change in the solvent (toluene/chain mixture). This is a tiny effect, though; the observed changes in $I(Q)$ originate in the star structure factor. The growing of low-Q intensity at higher c_{lin} conforms to the calculated compressibility increase upon adding linear polymer, in line with experimental findings in colloid-polymer mixtures [24].

These effects can be understood in terms of an effective potential $V_{\text{eff}}(r)$ acting between the stars in the presence of the chains, related to the star-star radial distribution function $g_{11}(r; \rho_1, \rho_2)$ through $V_{\text{eff}}(r)/(k_B T) = -\lim_{\rho_1 \rightarrow 0} \ln[g_{11}(r; \rho_1, \rho_2)]$ [16]. Results are shown in Fig. 4. The chains reduce the range of the bare star-star repulsion due to the *depletion* mechanism of the chains. Indeed, smaller chains cause an effective attraction between larger colloidal particles [20,24]. In the case at hand, the depletion attraction is superimposed on the soft repulsion among the stars, thus its dominant effect is to bring about a *reduced repulsion* among them. The range of the attraction increases with size ratio, thus the reduction of the repulsions becomes more pronounced as q grows, in line with the features seen in Fig. 2. As the
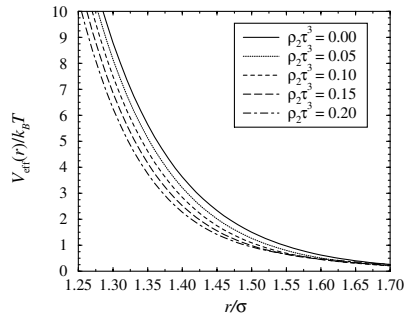
FIG. 4.   The effective, chain-mediated pair potential $V_{\text{eff}}(r)$ acting between the stars for size ratio $q = 0.30$ and for varying chain density, as indicated.

interstar repulsions become weaker, the correlations in the fluid are reduced and the latter regains stability.

In the high molecular weight limit, a gel-like behavior is recovered. The response of the mixtures in this regime is characterized by a time dependence, as it takes up to 3 h for the samples to reach dynamic equilibrium, depending on concentration and molecular weight. During this period, the moduli increase in value, maintaining the solid-like response at all times. We define a state of dynamic equilibrium as that in which the frequency response of the sample remains unchanged during two consecutive measurements 45 min apart. The frequency response of the mixtures indicates a solidlike response over three decades of frequency, and a weak power law of $G'(\omega)$ with exponents smaller than 0.5 and depending again on the linear polymer concentration and molecular weight. This is reminiscent of a dynamically percolated gel network, although in our case G'' is usually far from parallel to G'. For nearly all experiments, the concentration of linear chains is at or above its c_{lin}^{*}. In the liquid region the ratio $S = R_H^{\text{st}}/R_H^{\text{lin}}$ remains $S > 2$, whereas in the reentrant gel region we have $S \leq 1$. We argue then that the depletion mechanism, which in the range $S > 2$ is enhanced when S decreases, breaks down beyond a certain $S \sim O(1)$, where the linear chains cannot be described as ultrasoft spheres anymore. In that case, there is a large entropic cost for linear chains to penetrate the stars or even maintain their overall spherical shape (also dictated probably by osmotic reasons to equilibrate density fluctuations) and the large polymer chains form a transient physical network. This brings analogies to the bridging flocculation of conventional colloids, attributed to very long polymer chains which absorb to or attach on particles and form virtual physical networks [25].

The polymer-induced reduction of the star-star repulsions, the melting of the ultrasoft colloidal gel, and the subsequent reentrant gelation found here, are distinct from the recently found melting of a glass formed of hard spherelike microgel particles upon addition of chains [15,26]. As that effect has been attributed to chain-mediated attractions between the microgels, it has been qualitatively modeled by a square-well potential acting between the spheres [27]. Though we cannot rule

out a deep connection between the two, to be investigated by a mode coupling theory analysis, this attempt lies beyond the scope of our work which reveals that net attractions are not the only physical mechanism giving rise to such phenomena.

The addition of linear polymer chains to a multiarm star gel yields melting. This striking phenomenon offers unique opportunities to design and engineer novel nano-structured soft materials at the molecular level, leading to kinetic manipulation of the state of soft materials though additives, and achieving liquefaction or jamming. Moreover, it provides the framework for a thorough understanding and control of the interactions in soft matter physics, where macromolecular sizes and architecture critically influence the excluded volume, and thus, the entropic and kinetic character of phase transitions. Future efforts will focus on the derivation of realistic linear-chain–star interactions, in attempting to bring about quantitative agreement between theory and experiment.

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