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Solution properties of star polyelectrolytes having a moderate number of arms

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Abstract

We investigate polyelectrolyte stars having a moderate number of arms by molecular dynamics simulations of a coarse-grained model over a range of polyelectrolyte concentrations, where both the counter-ions and solvent are treated explicitly. This class of polymeric materials is found to exhibit rather distinct static and dynamic properties from linear and highly branched star polyelectrolyte solutions emphasized in past studies. Moderately branched polymers are particle-like in many of their properties, while at the same time they exhibit large fluctuations in size and shape as in the case of linear chain polymers. Correspondingly, these fluctuations suppress crystallization at high polymer concentrations, leading apparently to an amorphous rather than crystalline solid state at high polyelectrolyte concentrations. We quantify the onset of this transition by measuring the polymer size and shape fluctuations of our model star polyelectrolytes and the static and dynamic structure factor of these solutions over a wide range of polyelectrolyte concentration. Our findings for star polyelectrolytes are similar to those of polymer-grafted nanoparticles having a moderate grafting density, which is natural given the soft and highly deformable nature of both of these ‘particles’.

I. INTRODUCTION

Most polymers encountered in living systems are polyelectrolytes because of their solubility in water, and this broad class of polymers is also ubiquitous in commercial materials in which water solubility is required.^{1,2} Examples include hydrogels in diapers and gene delivery,³ thickeners in food industries,⁴ drug delivery,^{5,6} water purification agents,⁷ cosmetics,⁸ etc. While the study of linear chain polyelectrolyte solutions has been the subject of numerous studies^{9–14} and reviews,^{15–18} star polyelectrolytes are much less well understood.

The star architecture is the simplest branched polymer architecture where f linear chains are grafted on the surface of a core particle that has a size much smaller than the radius of gyration of the grafted chains. A better understanding for this particular polymer architecture is motivated by emerging applications of branched polyelectrolytes ranging from energy to medicine.² Moreover, star polyelectrolytes are also model systems in comparison with block

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copolymer micelles in aqueous solutions,^{19,20} colloids with polymer-grafted chains,^{21,22} and semi-flexible filamentous viruses,²³ which all involve polymer chains extending from a central core region.

Early experimental work on star polyelectrolytes indicated that they can form crystalline lattices near their overlap concentration.²⁴ This initially surprising observation led Pincus,²⁵ and others following him, to model the effective interaction between star polyelectrolytes by a coarse-grained model that emphasized the repulsive interactions deriving from the counterions surrounding polyelectrolytes. Subsequent experimental studies found that increasing the number of arms leads to enhanced crystal ordering,^{26–28} which was similar to the ordering observed for core-shell microspheres.^{29,30} Theoretical studies of star polyelectrolytes have mainly been limited to scaling arguments aimed at modeling the molecular conformation in these complex materials.^{19,31} Likos et al. achieved a more fundamental understanding of *highly branched star* polyelectrolytes through the development of a self-consistent effective pair-wise potential to describe the interactions of two polyelectrolyte stars,³² which allowed him to construct a phase diagram of the different crystal structures that formed with variation of the number of arms and the polymer concentration.^{33,34} However, there is limited understanding of the structure of star polyelectrolyte solutions having intermediate degree of branching, $2 < f < 20$, where no tendency towards crystallization seems to exist.

From a fundamental perspective, star polymers have attracted great interest due to the ability to “tune” the average molecular shape from the highly anisotropic linear chains to highly isotropic colloidal-like particles by increasing f .^{35,36} Specifically, a crossover from polymer to particle-like behaviors was observed for $f \approx 6$ for neutral polymers,^{36,37} and we expect a similar conformational transition to also arise in polyelectrolytes. Stars having a moderate value of f can naturally be expected to behave as “soft” particles exhibiting significant fluctuations in size and shape as in case of flexible polymers. Simulation studies of other soft particle systems such as polymer-grafted nanoparticles^{38–40} have indicated a tendency to form equilibrium disordered solids rather than crystalline materials because of the fluctuating effect of the conformational disorder packing having low compressibility as in the case of crystals. We may then expect polyelectrolyte stars having an intermediate number of arms to form soft amorphous solid. At high polymer concentrations, we also anticipate these materials to exhibit dynamical heterogeneities and growing relaxation times with increasing polymer concentration.

In the present work, we investigate the spatial organization of polyelectrolyte solutions with segmental concentration where the molecular architecture changes from highly anisotropic linear chains to isotropic highly branched star polyelectrolytes. Our investigation utilizes molecular dynamics (MD) simulations of a coarse-grained bead-spring chain model with an explicit solvent and we calculate the average size of the polyelectrolytes to have understanding of the relevant molecular-related length scales, and spatial correlations for quantifying the spatial organization of the polyelectrolytes in the solution. The polyelectrolyte solution structure is probed by calculating the segmental and center-of-mass static structure factor, as well as, the radius of gyration, hydrodynamic radius, the average molecular shape, and the center-of-mass structural relaxation time. Based on these results,

we rationalize the non-trivial structural variation of star polyelectrolytes exhibit with polyelectrolyte concentration and functionality.

Our paper is organized as follows. Section II contains details of the model and simulation methods. Results of the characterization of the size and shape, as well as, the structure of polyelectrolytes having different molecular topologies at different concentrations are presented in Section III. Section IV concludes the paper.

II. MODEL AND METHODOLOGY

We employ a bead-spring model of Lennard-Jones (LJ) segments bound by stiff harmonic bonds suspended in explicit LJ solvent particles, some of which are charged to represent counter-ions.^{41–44} Our model incorporates minimal aspects of real polyelectrolyte solution while at the same time it allows for equilibrated molecular dynamics with an explicit solvent. The added cost in computational time required by inclusion of an explicit solvent is necessary to fully capture the polyelectrolyte structural and dynamical behavior, as indicated by a series of studies.^{42,43} Moreover, simulation of the competitive binding of the solvent and counter-ions to the polyelectrolyte backbone, an essential feature of these molecules, requires an explicit solvent. Competitive binding of molecular species to macromolecules is known to greatly alter the phase behavior of polymer solutions,^{45,46} leading to often counter-intuitive phase behavior. Even greater complexity can be expected when associated species have long range interactions. The model we use was introduced previously to probe the coupling between the counter-ions and molecular structure, as well as, the quantification of the counter-ion cloud surrounding isolated flexible polyelectrolyte structures.^{47–49}

All macro-ion segments, dissolved ions, and solvent particles are assigned the same mass m , size σ , strength of interaction ϵ , and all dissolved ions are monovalent. We set ϵ and σ as the units of energy and length; the cutoff distance for LJ interaction potential is $r_c = 2.5 \sigma$. All polyelectrolytes have a molecular mass of $M_w = 41$, carrying a $-e$ charge per segment, where e is the elementary charge. A star polyelectrolyte is modeled as f linear chains, having M segments, are grafted on the surface of a core particle. Thus, by keeping $M_w = fM + 1 = 41$, we explore a wide range of molecular architectures ranging from linear chain polyelectrolytes having $f = 2$ and $M = 20$ to highly branched star polyelectrolytes having $f = 20$ and $M = 2$. For the purposes of this study, we investigate molecular structures that have $M_w = 41$ and $f = 2, 4, 8$, and 20 . The bonds between polymer segments are connected via a stiff harmonic spring, $V_H(r) = k(r - l_0)^2$, where $l_0 = \sigma$ is the equilibrium length of the spring, and $k = 1000 \epsilon/\sigma^2$ is the spring constant.

The system is composed of a total of $N = 256\,000$ particles in a periodic cube of side L and volume V . The system includes N_p polyelectrolyte molecules and $N_+ = N_p Z_p$ counter-ions, where Z_p is the total polyelectrolyte charge $Z_p = -M_w e$. All systems have neutral total charge. All charged particles interact via Coulomb potential (with a cut-off distance 10σ) and a relatively short range Lennard-Jones potential of strength ϵ , and the particle-particle particle-mesh method is used.⁵⁰ The systems were equilibrated at constant pressure and constant temperature conditions, i.e., reduced temperature $k_B T/\epsilon = 1$ (where k_B is Boltzmann's constant) and reduced pressure $\langle P \rangle \approx 0.1$, and the production run were

performed at constant temperature constant volume, maintained by a Nosé-Hoover thermostat. The Bjerrum length was set equal to $l_B = e^2 / (\epsilon_s k_B T) = 1.85 \sigma$, where ϵ_s is the dielectric constant of the medium. Typical simulations equilibrate for 4000 τ and data is accumulated over a 10000 τ interval, where $\tau = \sigma(m/\epsilon)^{1/2}$ is the MD time unit and the time step $\delta t = 0.005 \tau$.

In the present work, the dispersion interactions between different species were kept the same and equal to the strength of the van der Waals interactions (e) between the same species. In general the dispersion interaction between the ions and solvent can be either smaller or larger than van der Waals interactions between the solvent molecules and it is expected to influence dynamical and thermodynamical solution properties, e.g., when the solvent has a higher cohesive interaction polymer backbone, modeling hydrophilic and hydrophobic interactions via versa. Future work will focus on understanding the effects arising from the asymmetry of these interactions.

III. RESULTS & DISCUSSION

We first determine the average polyelectrolyte size of polymers having different molecular architectures as function of the polyelectrolyte concentration and at salt-free conditions. This provides a relevant characteristic length scale necessary to define when the polyelectrolytes start effectively overlap with each other. Following this analysis, we calculate the static structure factor for these systems and in particular probe the variation of the location of the primary peak as function of the concentration for different molecular architectures. Finally, we briefly study the dynamical behavior of polyelectrolytes that exhibit structural signatures of a “jamming” solution.

A. Effect of branching on polyelectrolyte size and shape

The polyelectrolyte segmental concentration is defined as, $\rho_{\text{seg}} = N_p M_w / V$ and has units σ^3 and correspondingly we define the charge fraction as, the ratio of charged particles over the total number of particles in the solution,

$$\varphi = (N_p Z_p + N_+) / N. \quad (1)$$

We shall see below that that the chain dimensions and segmental concentration can change even when the charge fraction φ is fixed. First, we calculate the ensemble average of the radius of gyration, $\langle R_g \rangle$, and the hydrodynamic radius, $\langle R_h \rangle$. The calculation of the latter is based on the use of path-integration algorithm ZENO, which allows for the facile calculation of the friction coefficient of arbitrarily shaped Brownian particles.^{51–53} An increase of ρ_{seg} results in a decrease in both $\langle R_g \rangle$ and $\langle R_h \rangle$; see Fig. 1a. In a previous paper,⁴⁹ we showed that the polyelectrolyte chains of the present model exhibit worm-like chain conformations rather than rod-like conformations in dilute polyelectrolyte solutions. We found that the equilibrium conformations of polyelectrolytes results from a balance of two effects derived from the coupling of the spatial distribution of counter-ions and the spatial distribution of the polyelectrolyte segments. In particular, counter-ions in the proximity of the polymer were found to be in two dynamical states, “condensed” counter-ions localized transiently near the

chain back-bone that alter the effective charge of the polymer,⁵⁴ and diffusely localized counter-ions within the space pervaded by the polymer chain that screen the effect of the residual charge of the polyelectrolyte – condensed counter-ion complex. There is a strong coupling between the chain conformation and the distribution of the condensed and diffusely localized counter-ions so that the more coiled nature of the polyelectrolyte chain cannot be attributed either solely to the reduced effective charge of the polyelectrolyte molecules or to the presence of charge screening by the charges within the polymer domain. In Figures 1 and 2, we also see the average hydrodynamic and static measures of polymer size as well as the average polymer shape (as estimated from $\langle R_h \rangle / \langle R_g \rangle$) also depend on the charge fraction, ϕ , but first we discuss the influence of varying molecular topology on the chain conformation and the overall solution density.

As in the case of uncharged polymers, polymer branching can greatly influence molecular size and solution properties, as illustrated in Fig. 1a. Increasing f for polyelectrolytes with fixed M_w leads not only to a significant decrease of $\langle R_g \rangle$, but a suppression of fluctuations in the magnitude of R_g . In particular, the variance of R_g for polyelectrolytes having a fixed molecular mass decreases as a power law in f^{-3} and this quantity is nearly independent of ρ_{seg} , see Fig. 1b. Fluctuations in R_g evidently become rather small for $f > 4$. This progressive decrease in the variance with f is also found for R_h , but to a smaller degree see Fig. 1a.

The ratio between R_h and R_g is often used as a descriptor of shape for particles and polymers.^{51,52} Specifically, R_h/R_g for a sphere equals 1.29, for a random walk is about 0.79, and for an infinite long rod R_h/R_g approaches 0.^{55,56} Intermediate values of this ratio can be taken as rough measure of polymer “asphericity” that is readily accessible through measurement. In our previous simulations^{48,49} and neutron scattering measurements using contrast matching methods,⁵⁷ polyelectrolyte chains were found to have a relatively “worm-like” chain configurations so that these polymers are stiffer than flexible polymers without charge interactions, but their shape is quite distinct from a rod. With an increase in polymer concentration ρ_{seg} , polyelectrolyte chains are found to not only become smaller (as discussed above), but also their average shape apparently becomes more symmetric. By keeping the molecular mass, M_w , of the star polyelectrolytes fixed, and by varying the number of arms f , we obtain significant changes in $\langle R_h \rangle / \langle R_g \rangle$ that correspond to a shape change from the limit of compact near-spherical structures for $f = 20$ to highly asymmetric semi-flexible polymer chains for $f = 2$; see Fig. 2. The fluctuations in this ratio do not decrease with increasing f as found in the case of R_g . Increasing f leads to molecular conformations that are more compact and spherically symmetric, as indicated in Fig. 2. A similar shape transition of stars in the melt was observed in a previous study of uncharged polymer in the melt.³⁶ While this polymer shape transformation in polyelectrolytes is not surprising in hindsight, there are strong implications for polyelectrolytes solution properties.

Density changes that accompany dissolving salts in water are among the earliest scientific observations and have provided significant insights into the nature of ion solvation and the thermodynamic and dynamic properties of aqueous solutions.^{58–60} The strong association of counter-ions and the solvent with the polymer backbone can be expected to likewise lead to changes in the solution density, an effect that should also be dependent on chain topology since the distribution of counter-ions generally topology dependent. Since we fix the total

number of particles was fixed and performed in our simulations at constant pressure and temperature, we can calculate these solvent density changes associated with the dissolution of polyelectrolytes. Fig. 3 shows that average the solution density, $\rho = N/V$, generally increases at low polymer concentrations from that of the pure solvent ρ_0 with increasing ρ_{seg} . However, this trend can change at higher polymer concentrations. For linear chains and stars having a moderate number of arms, ρ first exhibits a maximum and then becomes negative when $100 \rho_{\text{seg}}$ becomes greater than 5 to 6. As with aqueous salt solutions, the solution density is indeed not a simple concentration weighted average of the densities of the solution components.

These significant changes in the solution density upon adding polyelectrolytes in the solution indicate that we must distinguish between ρ_{seg} , which informs about the number of polyelectrolyte segments in a given volume, and the spatial charge distribution, describing the degree of the overlap between polyelectrolyte chains. This distinction is complicated by the fact that polyelectrolytes attract counter-ions, which are spatially distributed around the polymer chains in a non-uniform way.⁶¹ To address this phenomenon, we build on previous work quantifying the distribution of counter-ions in the limit of dilute polymer solutions. In particular, we found⁴⁷ that, the size of the (monovalent) counter-ion cloud around an isolated polyelectrolyte in moderate salt concentration is about $5/2$ times larger than R_g , meaning that polyelectrolytes along with their associated counter-ions can be viewed as soft “particles” having a size that is roughly twice their bare molecular size. Correspondingly, we define the average molecular volume a polyelectrolyte chain as in the case of uncharged

polymers, to be equal $\frac{4\pi}{3} R_g^3$, and the effective volume of the polyelectrolyte-counterion complex to equal $\frac{4\pi}{3} (2R_g)^3$. This later measure of the size of a polyelectrolyte chains motivates the definition of an effective polyelectrolyte solution concentration,

$$\phi_{\text{eff}} = \frac{4\pi}{3} \frac{N_p (2R_g)^3}{V} = \frac{4\pi}{3} \frac{\rho_{\text{seg}}}{M_w} (2R_g)^3. \quad (2)$$

We find that ϕ_{eff} scales linearly with polyelectrolyte concentration in dilute polyelectrolyte solvents, but ϕ_{eff} scales with a smaller power consistent within numerical uncertainty with the scaling, $\phi_{\text{eff}} \propto \rho_{\text{seg}}^{1/3}$ at higher ρ_{seg} solutions. This crossover is more noticeable for linear chains and for star polyelectrolytes having a small number of arms, while for larger f only the former scaling is observed. This crossover seems to be very general, and based on the assumption of this universality, we fit ϕ_{eff} to a function exhibiting this crossover scaling,

$$\phi_{\text{eff}} = \frac{\gamma(f) \rho_{\text{seg}}}{[1 + \rho_{\text{seg}} / \rho_{\text{seg}}^*(f)]^{1.29}}, \quad (3)$$

where

$$\gamma(f) \approx 1622.79 f^{-2} \quad (4)$$

and

$$\rho_{\text{seg}}^*(f) \approx 0.0078 \exp(f^{0.66}/0.955). \quad (5)$$

Despite the significant variation in concentration and in molecular structure, Eqs. 3, 4, and 5 quantify the relation between the ϕ_{eff} and ρ_{seg} by capturing the effects of molecular size and its variation with segmental concentration. In particular, the function $\gamma(f)$ reflects an effective reduction in size due to the increase in f . Higher values of $\rho_{\text{seg}}^*(f)$ shift the crossover at higher concentrations and enlarging the concentration regime at which $\phi_{\text{eff}} \propto \rho_{\text{seg}}$. In other words, it reflects the “plasticity” of the molecules to respond to changes in the polyelectrolyte concentration. Eqns. 2 and 3 can be further used to obtain a R_g scaling relation as function of ρ_{seg} :

$$R_{g,\text{pred}} = \frac{R_{g,0}}{[1 + \rho_{\text{seg}}/\rho_{\text{seg}}^*(f)]^{0.43}}, \quad (6)$$

where $R_{g,0}$ corresponds to R_g of a polyelectrolyte at $\rho_{\text{seg}} \rightarrow 0$,

$$R_{g,0} = \frac{1}{2} \left[\frac{3M_w \gamma(f)}{4\pi} \right]^{1/3}. \quad (7)$$

A direct comparison between the predicted values of radius of gyration and the values obtained from the simulations is presented in the inset of Fig. 4. The functional form of Eq. 6 has the same form frequently employed in solutions of neutral polymers, where the concentration exponent defining the screening of the polymer self-excluded volume interactions depends on chains stiffness and topology.⁶² The mutual screening of the charge and excluded volume interactions in polyelectrolytes evidently depends on additional molecular parameters that influence the distribution of counter-ions around the polyelectrolyte and charged segments within the chain, as well as excluded volume interactions. The selective affinity of the counter-ions for the solvent or the solvent for the polymer backbone are probably highly relevant to this charge screening effect in polyelectrolytes generally and this potentially relevant variable need to be studied in future simulations of our polyelectrolyte model.

B. Structure of polyelectrolyte solutions

Now that we have identified the relevant length scales and the effective polyelectrolyte concentration, we focus on understanding the structural nature of polyelectrolytes in solutions based on our polyelectrolyte model. The static structure factor, $S(q)$, is a suitable

property for this purpose and describes the mean correlations in the positions of the polyelectrolytes. For a collection of point particles, $S(q)$ is defined as:

$$S(q) = \frac{1}{N_s} \left\langle \sum_{j=1}^{N_s} \sum_{k=1}^{N_s} \exp[-i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_k)] \right\rangle, \quad (8)$$

where $i = \sqrt{-1}$, $q = |\mathbf{q}|$ is the wave number, $\mathbf{r}_j$ is the position of particle j , $\langle \rangle$ denote the time average, and N_s is the total number of polyelectrolyte segments defined as $N_s = N_p (fM + 1)$. $S(q)$ of linear chain polyelectrolytes in solution has received considerable attention over the last two decades with a primary focus on polyelectrolyte chains like DNA and other highly charged molecules.^{9,63–67} Several interesting features are observed in the static structure factor $S(q)$, both in simulation and experimental studies. Specifically, at relative low concentrations, we observe a primary peak of polyelectrolytes in the structure factor, suggesting strong spatial correlations on a length scale on the order of the size of the molecules. The resulting $S(q)$ for polyelectrolyte solution at different concentrations confirm this description, as seen in Fig. 5. We find some common features in $S(q)$ with variation of molecular architecture. For example, for all molecular architectures we find that at large length scales the values of $S(q)$ decrease with concentration suggesting that spatial fluctuations between polyelectrolytes are greatly suppressed. We continue our discussion with the behavior of this liquid-like ordering with variation of concentration and molecular architecture.

Considerable attention has been placed in understanding the scaling of the “primary peak” position, q_{peak} , in $S(q)$ with polymer concentration, ρ_{seg} . Most experiments for linear chain polyelectrolytes show that q_{peak} scales with a power law exponent near 1/3 in dilute solutions and approximately 1/2 in semidilute solutions.^{64,68} The exponent 1/3 represents the tendency of particles spatially localizing at interparticle distances. Since the particle concentration being proportional to their volume fraction, this behavior is typical in charged colloidal-like particles (as discussed below). Polyelectrolyte chains in dilute solution are often observed to follow this scaling rather well, meaning that in dilute regime the polyelectrolyte chains can be effectively represented as point soft particles with long-ranged interactions. For semi-dilute polyelectrolyte chain solutions, scaling theories⁶⁹ predict $q_{\text{peak}} \sim \rho_{\text{seg}}^{1/2}$, which is consistent with simulation⁶⁵ and experimental studies.^{64,70}

Although scaling theories has rationalized this exponent, the peak broadens and shifts to higher q -values as the concentration is increased, suggesting that this “liquid-like” local ordering progressively decreases with increasing concentration. There has been considerable theoretical effort to understand this variation in peak position, however, there is no agreed interpretation of this trend.^{9,10,64,71} In our simulations, we find a scaling $q_{\text{peak}} \sim \rho_{\text{seg}}^{0.44}$, which is intermediate between the scaling for linear chain polymers and particle structures (see Fig. 6). It is noted that if we compare the exponents by considering only the three lowest and highest concentrations, then we obtain 0.43 and 0.46, respectively; this suggests that there is slow variation in the exponent from the dilute to semi-dilute concentration regimes.

Scaling arguments for polyelectrolyte solutions have predicted a concentration exponent of $1/2$, but these arguments assume that polyelectrolyte solutions are *structurally homogeneous*. In contrast, many low angle neutron and x-ray scattering measurements on polyelectrolyte solutions indicate the presence of large excess scattering at low q , corresponding to some kind of large scale heterogeneity.^{66,72–76} Moreover, the measured exponents, while often near $1/2$, are observed to lie in a range between $1/3$ and $1/2$.^{66,72–76} Preliminary calculations of this effective concentration scaling exponent based on our polyelectrolyte model, where we allow the solvent to have a preferential affinity for the polymer backbone and/or the counter-ions, indicate that both of these factors can greatly influence the homogeneity of the polymer solution, as well as the concentration scaling exponent of the polyelectrolyte peak. The scaling of the polyelectrolyte peak position with polymer concentration would appear to be *non-universal*, depending on the many physical factors affecting the association of the polyelectrolytes in solution. This phenomenon obviously deserves further study from computational and experimental standpoints.

Star polyelectrolytes evidently exhibit a much richer behavior than their linear chain counter-parts. For all concentrations explored, star polyelectrolytes having $f=8$ and 20 scale as $q_{\text{peak}} \sim \rho_{\text{seg}}^{1/3}$. This means that no discoverable crossover from “dilute” to “semi-dilute” regimes as in flexible polymer solutions. This change of behavior is also observed in charged colloids at low ionic strength, where the colloids maximize their average interparticle distance, meaning that the characteristic length scale defined again by the peak in $S(q)$ depends in the volume fraction to the $1/3$ power. A similar variation has been observed for charged dendrimers,^{77–79} copolymer micelles,^{20,80} porcine stomach mucins⁸¹ and proteoglycan monomers from cartilage,⁸² overall this suggests that this scaling is rather widely observed. We note that the exponent of the concentration scaling for star polyelectrolytes having $f=20$ is slightly smaller $1/3$; specifically, we find an exponent of approximately 0.28. This suggests that the addition of ionic species has a smaller impact on the characteristic length scale (i.e., $2\pi/q_{\text{peak}}$). This is not unreasonable, since an increase in ion concentration results in the screening of the Coulomb interactions and thus leading to a weakening the repulsive interactions between the polyelectrolytes. In other words, the q_{peak} dependence with concentration has a non-trivial behavior due to the screening of charge interactions.

For $f=4$ stars, we find a scaling of $q_{\text{peak}} \sim \rho_{\text{seg}}^{1/3}$ at concentrations below $100 \rho_{\text{seg}} \approx 2$, consistent with stars acting as independent particles. However, above this threshold there is a relative abrupt crossover in q_{peak} scaling and exhibits a behavior similar to polyelectrolyte chains. In other words, the particle-like character of star polyelectrolytes observed at low concentrations changes to a behavior characteristic of flexible chains at higher concentrations. A closer examination of $S(q)$ in Fig. 7 indicates that near the concentration threshold of this crossover there are two peaks in $S(q)$. While at low concentrations there is a single primary peak reflecting the intermolecular distance, just below this threshold the primary peak is accompanied by a shoulder located at slightly higher q -values, reflecting the distance between the arms of different polyelectrolyte stars. This shoulder becomes more prominent as the primary peak becomes smaller. At the polyelectrolyte concentration threshold, the primary peak and the shoulder have nearly the same height. The shoulder

becomes the primary peak at higher values of ρ_{seg} , resulting in a change of q_{peak} dependence on concentration. To the best of our knowledge, this crossover from particle-like to linear chain-like behavior in polyelectrolyte stars has not been reported before.

While we observe the well known peak broadening effect for linear chain polyelectrolytes, polyelectrolyte stars having $f=20$ exhibit a primary peak that shifts to larger q -values while the peak narrows and becomes more pronounced. This is evidence for an enhanced local ordering with increasing polymer concentration; see Fig. 5. Interestingly, star polyelectrolytes having $f=8$ exhibit an intermediate behavior between these two extreme behaviors. Specifically, while the overall trend follows that of linear polyelectrolytes, i.e., the peak broadens with concentration, we find a concentration range in which the peak follows the trends of highly branched star polyelectrolytes, $1 \gtrsim 100 \rho_{\text{seg}} \gtrsim 3$, see Fig. 5.

To better understand this enhancement of the local ordering between the polyelectrolyte segments, we calculate the static structure factor of the polyelectrolyte center of mass $S_{\text{CM}}(q)$,

$$S_{\text{CM}}(q) = \frac{1}{N_p} \left\langle \sum_{j=1}^{N_p} \sum_{k=1}^{N_p} \exp[-i\mathbf{q} \cdot (\mathbf{r}_{\text{cm},j} - \mathbf{r}_{\text{cm},k})] \right\rangle, \quad (9)$$

where $i = \sqrt{-1}$, $q = |\mathbf{q}|$ is the wave number, $\mathbf{r}_{\text{cm},j}$ is the position of the center of mass of polyelectrolyte j , $\langle \rangle$ denote the time average. Our observations for a dense polyelectrolyte solution are presented in Fig. 8a. Here, we utilize the semi-empirical Hansen-Verlet freezing rule,⁸³ which states that “freezing” occurs when the height of the primary peak of $S_{\text{CM}}(q)$ is about 2.85 in three dimensions. In physical terms, the polymers become “jammed” by their neighbors, leading to a tendency towards polymer localization. This criterion is helpful in roughly locating the freezing and melting lines for a given system and without free-energy calculations. Evidently, we find polyelectrolytes having $f=8$ and 20 exhibit signatures of jamming from not only from the height of the primary peak, but also from the tendency of the secondary peak to split. This is particular clear in the case of $f=20$ arms and examining the radial distribution function of the center of mass, $g_{\text{CM}}(r)$. In the inset of Fig. 8, we illustrate the normalized $g_{\text{CM}}(r)$, where the first peak is located at distance $r/r_0 = 1$ and $r_0 \approx 8.5 \sigma$. Evidently, the second peak splits in to two peaks located at $r/r_0 \approx \sqrt{3}$ and 1.95. These peaks correspond to triangular and collinear configuration of neutral hard spheres within randomly closed packed structures,^{84–86} which suggests that dense concentrated polyelectrolyte stars having $f=20$ arms exhibit structural characteristics that are similar to jammed hard spheres having an effective size, $r_0 \approx 8.5 \sigma$. At $\phi = 0.256$, the density fluctuations are significantly suppressed for all molecular architectures, and $S(q)$ goes towards values near zero as $q \rightarrow 0$. These observations confirm our expectations that polyelectrolyte stars with a moderate degree of branching form *glassy materials* rather than crystals at high polymer concentrations.

To capture the structure behavior of the polyelectrolyte center of mass spatial organization, we constructed a map based on the Hansen-Verlet freezing rule, see Fig. 8b. There are two

regimes, the first one is the liquid-like ordering between the center of mass of polyelectrolytes and it has the height of the primary peak in $S_{CM}(q)$ is $S_{CM}(q) < 2.85$. This regime occurs for low concentration polyelectrolyte solutions irrespectively of molecular architecture and for low f polyelectrolyte stars (including linear chains), irrespectively of concentration. The second regime occurs for high concentration solutions having highly branched stars. Interestingly, more arms do not necessarily increase the ordering in the solution for a given concentration. For $100 \rho_{seg} \approx 4$, we find that $f=8$ stars have a higher degree of ordering than $f=20$. A possible interpretation behind this is that while an increase in f results in a more compact molecular structure and by extension a ‘stiffer’ effective potential interaction, but at the same time the range of this interaction decreases which in turn reduces the frustration and the degree of order in dense polyelectrolyte solutions. This result reflects the non-trivial dependence of the effective interactions with molecular architecture.

C. Dynamical evidence for amorphous solidification in star polyelectrolytes having a moderate number of arms

Overall, the results in Figs. 5 and 6 clearly show that there is a very rich range of structural variation in the $S(q)$ with variation of concentration and molecular architecture. Many of our findings were not been addressed previously in the literature and highlight the crucial role of molecular architecture in the structural organization of polyelectrolytes. Before concluding, we briefly examine the consequence of these structural changes in the *dynamics* of polyelectrolyte stars having a moderate number of arms. We probe the polyelectrolyte dynamics through the considerations of density fluctuations and the dynamical extension of the static structure factor, from which the structural relaxation time τ_α can be obtained. There is a large literature focusing on τ_α in the study of glass-forming liquids and we draw on this literature here.^{36,87–89}

Our analysis begins with a consideration of how the molecular architecture of the polyelectrolytes influence the dynamics. To this end, we first calculate the self-intermediate scattering function:

$$F(q, t) = \frac{1}{N_p} \left\langle \sum_{j=1}^{N_p} \exp \{ -i\mathbf{q} \cdot [\mathbf{r}_{cm,j}(t) - \mathbf{r}_{cm,j}(0)] \} \right\rangle, \quad (10)$$

where $\mathbf{r}_{cm,j}(t)$ is the position of the center of mass of polyelectrolyte j at the time t . The structural relaxation time τ_α may defined as $R(q) = q_{peak}$, $t = \tau_\alpha = 1/e$, where e is the Euler’s constant.

The resulting $R(q, t)$ curves are presented in Fig. 9. In particular, we find that $R(q, t)$ for linear chain polyelectrolytes decays more quickly with *increasing* concentration. This is an unexpected trend since in neutral polymers in solution the relaxation always increases with concentration. Previous theoretical efforts rationalized this counter-intuitive trend as being due to counter-ion condensation.^{90–93} We find a similar behavior for star polyelectrolytes having $f=4$ arms. However, for star polyelectrolytes having $f>4$ arms, we observe a

significant change in behavior of $R(q, t)$, reflecting structural changes in the polyelectrolyte solution. Specifically, we find that there is a speeding up of the decay of $R(q, t)$ at low concentration solutions as in linear chain polyelectrolyte solutions, but beyond a concentration threshold the decay of $R(q, t)$ slows down; compare the arrows in Fig. 9. Evidently, the polyelectrolyte stars become trapped by their neighbors, leading to frustrated dynamics. This behavior is again reminiscent to the dynamics of glass-forming liquids where the neighboring particles form a “cage” and effectively restrict the particle mobility. In polyelectrolyte solutions, the caging arises from the long-range Coulomb interactions of neighboring polyelectrolytes, and while the polyelectrolytes exhibit dynamics akin to glass-forming materials the solvent (neutral) particles move through the polyelectrolytes without exhibiting this slowdown in dynamics. The frustrated dynamics with concentration become stronger for star polyelectrolytes having $f = 20$. It would appear that these soft polymers having a moderate number of arms tend to form a glass-like state rather than a crystal structures at high polyelectrolyte concentrations.

To better understand the dynamics of polyelectrolytes having different branching architectures with the variation of ρ_{seg} , we probe the structural relaxation time τ_a as function ρ_{seg} as seen in Fig. 9. For linear chain polyelectrolytes, we find τ_a to scale with a power law as $\rho_{\text{seg}}^{-0.76}$. Polyelectrolyte stars having $f = 4$ arms exhibit slower dynamics at low concentrations $100 \rho_{\text{seg}} < 3$, however, at higher concentration the stars relax nearly the same way as linear chain polyelectrolytes. This dynamical crossover coincides with the structural crossover in the q_{peak} dependence with concentration, see Fig. 6. For polyelectrolyte stars with $f > 4$, however, we find that the dynamics slow down considerably for concentrations $100 \rho_{\text{seg}} > 2$. Specifically, for $\phi = 0.256$ the ratio of structural relaxation times for highly branched stars $f = 20$ over linear chain polyelectrolytes $f = 2$ is $\tau_a(f = 20)/\tau_a(f = 2) \approx 85$, meaning that the dynamics slow down by a factor of 85 times by increasing f from 2 arms to 20 arms. This finding is counter-intuitive, given that the only difference between these two systems is the segmental connectivity, i.e., molecular architecture. Overall, these results highlight the richness of structural and dynamical behaviors exhibited by star polyelectrolytes having a moderate number of arms, making this class of polymers an excellent model system for the design of new “soft” polymeric materials.

IV. CONCLUSIONS

In summary, we use molecular dynamics simulations to investigate the structural organization of salt-free linear chain and star polyelectrolyte solutions as function of polyelectrolyte concentration. As in the case of un-charged star polymers,³⁶ polyelectrolyte stars undergo an average shape crossover from highly anisotropic linear chain polyelectrolytes to particle-like structures with an increasing number of star arms, f . This structural transition arises in both classes of polymers for relative small $f \approx 4$ arms to 6 arms. Previous work has shown that stars with a large number of arms,^{33,34} highly branched polymeric structures,^{38,94,95} and high generation of dendrimers^{77–79} tend to crystallize at relative low concentrations, as in the case of charged colloidal spheres.^{96–101} However, stars with an intermediate number of arms $2 < f < 20$ form dynamically heterogeneous materials at high polyelectrolyte concentrations because of packing frustration arising from the shape

and size fluctuations of these polyelectrolytes. We quantify the onset of this transition by calculating the static and dynamic structure factors of star polyelectrolytes solutions over the range of concentrations accessible by equilibrium simulation and observe the onset of local intermolecular “jamming” from the growth in the height of the primary peak in the static structure factor $S(q)$ and the strong suppression of $S(q)$ in the long wavelength limit $q \rightarrow 0$, implying the reduction of the fluid compressibility.^{102–104} Similar trends have been observed in polymer-grafted nanoparticles having a moderate grafting density where this effect is especially large.⁴⁰ The dynamics of both polyelectrolyte stars having inter-mediate number of arms and moderately polymer-grafted nanoparticles show sharp slowing down with increasing concentration that is symptomatic of incipient solidification. Sciortino and coworkers¹⁰⁵ have recently shown that nanoparticles with a moderate number of grafted DNA chains can form an equilibrium amorphous state in which the crystalline state is metastable. We expect the same situation to arise in soft star polyelectrolyte stars having a moderate number of arms. This class of polyelectrolytes should then have unique properties in comparison to the previously studied cases of linear chain and highly branched star polyelectrolytes and these polymer deserves consideration as a candidate materials from creating unique “soft” materials.

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FIG. 1.

(a) Average radius of gyration, $\langle R_g \rangle$, and hydrodynamic radius $\langle R_h \rangle$ as function of the segmental concentration, ρ_{seg} , for polyelectrolytes having different molecular architectures with molecular mass, $M_w = 41$. The uncertainty estimates represent one standard deviation. The dot-dashed lines correspond to systems having the same charge fraction, $\phi = (N_p Z_p + N_+)/N = 0.128$ and 0.256 . (b) Variance of radius of gyration, $X(R_g)$ as function of functionality, f ; results for different concentrations are also presented. The dashed line is power law scaling as f^{-3} . (c) Screenshots of polyelectrolytes having different molecular architectures.

FIG. 2. Ratio of the average hydrodynamic radius over the average radius of gyration, $\langle R_h \rangle / \langle R_g \rangle$ as function of the segmental concentration, ρ_{seg} , for polyelectrolytes having different molecular topologies. The uncertainty estimates represent one standard deviation. The symbols are the same as in Fig. 1.

FIG. 3.

Average deviations of the solution density as function of the polyelectrolyte segmental concentration, ρ_{seg} . The reference point of the solution density is the solution density of a pure solvent, ρ_0 .

FIG. 4.

Scaled effective volume fraction, ϕ_{eff} , as function of scaled segmental density, ρ_{seg} . The dashed line corresponds to Eq. 3. Inset: polyelectrolyte radius of gyration predicted by Eq. 6, $R_{g,\text{pred}}$, as function of the average radius of gyration, $\langle R_g \rangle$, calculated from the simulations; results for all polyelectrolyte concentrations investigated here are presented. The dot-dashed line is a linear relation of $R_{g,\text{pred}} = \langle R_g \rangle$.

FIG. 5.

(Left) Static structure factor, $S(q)$ for linear chain polyelectrolytes at different molecular architectures and charge fractions, $\phi = 0.032$ (continuous black line), 0.064 (dashed red line), 0.128 (dash-dot green line), and 0.256 (dash-double-dot green line). Arrows highlight the behavior of the height of the primary peak of $S(q)$ with increasing polyelectrolyte concentration. (Right) Screenshots of the polyelectrolyte solutions for stars having $f=2$ and 20 at different concentrations. The solvent particles are rendered invisible for visualization purposes.

FIG. 6. Location of the primary peak q_{peak} in the static structure factor $S(q)$ as function of the polyelectrolyte segment concentration, ρ_{seg} . The arrow points to the crossover of polyelectrolytes having $f=4$ arms from the particle-like behavior (low concentration) to linear chain-like behavior at higher concentrations. Inset: q_{peak} as function of functionality for two charge fractions, $\phi = 0.032$ (filled circles) and $\phi = 0.256$ (filled squares).

FIG. 7.

Segmental static structure factor of polyelectrolytes having $f=4$ arms at different concentrations near the crossover between particle-like behavior to chain-like. This crossover is near $100\rho_{\text{seg}} \approx 3.2$, also see the arrow in Fig. 6.

FIG. 8.

(a) Static structure factor of the polyelectrolyte center of masses, $S_{CM}(q)$, with charge fraction, $\phi = 0.256$, at different molecular architectures. The dashed line represents the Hansen-Verlet freezing rule,⁸³ $S_{CM}(q) = 2.85$. Inset: Normalized radial distribution function of the center of mass, $g_{CM}(r)$, of polyelectrolytes having $f=20$ and $\phi=0.256$. (b) Morphology map of star polyelectrolytes having fixed molecular mass and f number of arms with variation of the polyelectrolyte segmental concentration, ρ_{seg} . The symbols represent polyelectrolyte solutions that have the polyelectrolyte center of mass structure factor primary peak below (open circles) and above (crosses) the Hansen-Verlet freezing rule $S_{CM}(q) =$

2.85; the highlighted area approximately draws the boundary between these two type of solutions.

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FIG. 9.

(Left) Self-intermediate scattering function, $F(q, t)$, as function of time for different molecular architectures and charge fractions, $\phi = 0.032$ (continuous black line), 0.064 (dashed red line), 0.128 (dash-dot blue line), 0.192 (dash-double-dot green line), and 0.256 (dot-double-dash magenta line). The arrows show how the $F(q, t)$ curves decay with increasing the polyelectrolyte segmental concentration ρ_{seg} . (Right) Structural relaxation time τ_α as function of ρ_{seg} ; results for different molecular architectures are also presented. The dot-dashed lines correspond to systems having the same ϕ .