ABSTRACT: We investigate the effects of polymer molecular weight on the structure and dynamics of a model colloid–polymer bridging system using confocal microscopy. Polymer-induced bridging interactions between trifluoroethyl methacrylate-co-tetra-butyl methacrylate (TtMA) copolymer particles and poly(acrylic acid) (PAA) polymers of molecular weight $M_w$ of 130, 450, 3000, or 4000 kDa and normalized concentrations $c/\phi^*$ ranging from 0.05 to 2 are driven by hydrogen bonding of PAA to one of the particle stabilizers. At a constant particle volume fraction $\phi = 0.05$, the particles form clusters or networks of maximal size at an intermediate polymer concentration and become more dispersed upon further addition of polymer. Increasing the polymer $M_w$ at a fixed normalized concentration $c/\phi^*$ increases the cluster size: suspensions with 130 kDa polymer contain small clusters that remain diffusive, and those with 4000 kDa polymer form larger, dynamically arrested clusters. Biphasic suspensions with distinct populations of disperse and arrested particles form at low $c/\phi^*$, where there is insufficient polymer to bridge all particles, or high $c/\phi^*$, where some particles are sterically stabilized by the added polymer. Thus, the microstructure and dynamics in these mixtures can be tuned through the size and concentration of the bridging polymer.

INTRODUCTION

Suspensions composed of micrometer-sized colloidal particles and polymers are widely used in personal care and food products,1 3-D printing processes,2,3 and pharmaceutical manufacturing.4 The microscopic structure and hence macroscopic properties of these suspensions can be tuned by controlling the suspension composition via the particle and polymer concentrations and through the interactions between the particles and polymers. Nonadsorbing polymers induce interparticle depletion attractions.5,6 Adsorbing polymers, however, can generate steric repulsions when the polymers are short, or bridging attractions if the polymers are long enough to overcome electrostatic repulsions and form bridges between two particles.8 Further, when the surfaces of particles become fully saturated with adsorbed polymer, addition of polymer can also lead to depletion attractions.9,10 Thus, particulate suspensions containing adsorbing polymers exhibit a rich phase behavior, including flocs and networks. Flocculation processes driven by polymers or macromolecules adsorbed to the particle surface appear in filtration applications,11,12 beer fermentation,13,14 and rapid diagnostics for infectious diseases.15,16 Bridging interactions are also observed in suspensions of grafted nanoparticles or nanoemulsions, for which the solvent condition for chains,17 grafting density,18 bridging mecha-

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polymers as well as polymer concentration and molecular weight. In kaolin–polyethyleneimine suspensions, increasing the polymer concentration reduced the density and increased the fractal dimension of clusters; increasing the polymer molecular weight promoted bridging interactions between particles and polymers but did not strongly affect the yield stress. In kaolin–polyacrylamide suspensions, an increase in the polymer molecular weight slightly increased the cluster size and reduced the fractal dimension of flocs. In poly styrene–polydiallyldimethylammonium suspensions, increasing the polymer molecular weight led to greater surface coverage by the bridging polymers. In suspensions of silica particles and poly(ethyleneimine) polymers, the yield stress was greatest for the highest polymer molecular weight. Suspensions of silica particles and poly(acrylic acid) polymers exhibited shear thickening when the polymer molecular weight was sufficiently high to allow particles to be bridged by flexible coils; intriguingly, the suspensions with the highest polymer molecular weight ($M_w = 7.5 \times 10^5$ g mol$^{-1}$) did not shear-thicken because the long adsorbed polymers desorb before they are fully extended by the flow. In suspensions of silica particles and poly(ethyleneimine) polymers, the greatest yield stress was observed for the largest polymer ($M_w = 70,000$ g mol$^{-1}$). Most experiments, therefore, have focused on the effects of the particle–polymer size ratio on macroscopic (flow) properties. How the polymer size affects the microscopic structure and dynamics remains incompletely understood.

Confocal microscopy experiments allow particles to be visualized at the microscopic scale and thus provide an intriguing option for investigating the microscopic structure and dynamics of bridging suspensions. Only a few studies, however, have applied this method to investigate the behavior of suspensions with polymer-mediated bridging interactions. Confocal imaging on suspensions of clay, bitumen, and an anionic polymer flocculant revealed qualitative changes in the density and packing of flocs with increasing polymer concentration. Single-particle tracking experiments on silica–polyethylene suspensions showed that the microstructure and dynamics of these suspensions varied strongly with particle and polymer concentration: below a critical polymer concentration at which the maximum storage modulus was observed, suspensions contained both mobile (disperse) and arrested (aggregated) particles. How polymer molecular weight affects the microscopic properties of bridging suspensions has not been explored, to our knowledge, and is the focus of this study.

Using fluorescence confocal microscopy, we show that the polymer molecular weight affects the microscopic structure and dynamics of colloid–polymer bridging systems. We synthesized core–shell copolymer particles that were sterically and electrostatically stabilized through grafted polymers on the particle surface and that could be refractive-index-matched to 80(w/w)% glycerol–water. Bridging interactions are induced by the addition of poly(acrylic acid) (PAA), which forms hydrogen bonds with the steric and electrostatic polymer brush stabilizers. In our previous study, we showed that the structure and dynamics of these suspensions could be tuned through the pH-dependent bridging interactions. In this study, we characterized the microscopic structure and dynamics of suspensions at a constant particle volume fraction $\phi = 0.05$ containing PAA of various molecular weights (130, 450, 3000, and 4000 kDa) at normalized polymer concentrations $c/c^*$ (where $c^*$ is the polymer overlap concentration) ranging from 0.05 to 2. For all four $M_w$, metrics for particle structure and dynamics exhibit nonmonotonic trends as a function of $c/c^*$, consistent with a growing fraction of sterically stabilized polymers above a threshold concentration. Increasing the molecular weight of PAA at a fixed $c/c^*$ generally leads to the formation of larger clusters, likely due to the larger polymer radius of gyration. Finally, distinct populations of free and aggregated particles are obtained at $c/c^* = 0.05$ for all four polymers and at high $c/c^*$ for the two highest molecular weight polymers. Thus, the polymer $M_w$ provides additional control over the structure and dynamics of polymer-bridged colloidal suspensions.

### MATERIALS AND METHODS

**Copolymer Particle Synthesis.** All chemicals for particle synthesis were purchased from Sigma-Aldrich unless specified otherwise. Poly(2,2,2-trifluoroethyl methacrylate-co-tert-butyl methacrylate) (TtMA) particles were synthesized using previously reported procedures. Briefly, we first synthesized fluorescent particle cores, then grew a nonfluorescent shell, and finally grew charged stabilizer polymers on the particle surface using atom transfer radical polymerization (ATRP). A volumetric ratio of 45:55 of 2,2,2-trifluoroethyl methacrylate (TFEMA; SynQuest Lab) to tert-butyl methacrylate (tBMA) was used to obtain TtMA copolymer particles of diameter 1.63 ± 0.03 μm that were density-matched and refractive-index-matched to 80(w/w)% glycerol–water. Rhodamine B methacrylate was incorporated during core synthesis for confocal imaging. 2-(2-Bromoisobutyloxy)ethyl acrylate (initiator monomer) was added during core and shell synthesis as a growth initiator for addition of charged polymer on the particle copolymer surface. In that final synthesis step, a negatively charged copolymer composed of 2-acrylamidomethyl-1-propanesulfonic acid and dimethylacrylamide was grown on the copolymer particle surface via ATRP using a 1:1 input ratio of methanol:water. The charged copolymer particles were collected and washed using Millipore water and centrifuged five times at 738g for 5 min to remove any unreacted reagents. After the final centrifugation, glycerol was added to the particle pellet to obtain a stock of $\phi = 0.46$ in 60(w/w)% glycerol–water. The particle stock was centrifuged for 2.5 h, after which glycerol was added to obtain a particle volume fraction of $\phi = 0.49$ in 80(w/w)% glycerol–water. The stock was mixed once more and then centrifuged at 2000g for 3 min to remove bubbles that appeared during mixing. The glass vial containing the particle stock was sealed with Parafilm and stored in an explosive-proof refrigerator.

**Particle Characterization.** The hydrodynamic diameter $d_h$ of the TtMA copolymer particles in water was measured using dynamic light scattering (DLS) on a 3-D LS spectrometer (LS Instruments; Switzerland). Five correlation functions per angle were collected for 60 s at scattering angles of 30°, 60°, 90°, 120°, and 150°. The internal temperature was held constant at 25 °C. The correlation functions were fitted using a single exponential decay cumulant,

$$g^{(2)}(\tau, q) - 1 = \beta \exp(-2\Gamma q \tau)(1 + \frac{\mu_2}{2} q^2)$$

where $\beta = 1$ is a correction factor that depends on the instrumental scattering geometry, $\Gamma(q)$ is the average decay rate, $\tau(q)$ is the exponential decay time, $\mu_2$ is the second moment of the distribution, and $q$ is the scattering vector ($q = \frac{4\pi n}{\lambda}\sin(\theta/2)$). For $q, n = 1.333$ is the refractive index of...
Table 1. PAA Properties: Viscosity Average Molecular Weight $M_v$, Polymer Radius of Gyration $R_g^p$ Size Ratio $R_g^p/a$ (Using Particle Radius $a = d_{50}/2 = 815$ nm), Overlap Concentration $c^*$, Linear Configuration Contour Length $L_{v,l}$ and Tetrahedral Configuration Contour Length $L_{v,t}$

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<th>$R_g^p/a$ ($\times 10^{-2}$)</th>
<th>$c^*$ (mg mL$^{-1}$)</th>
<th>$L_{v,l}$ (nm)</th>
<th>$L_{v,t}$ (nm)</th>
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Sample Preparation. Stock suspensions of TtMA copolymer particles in glycerol–water and aqueous solutions of PAA were combined to produce colloid-polymer suspensions at volume fraction $\phi = 0.05$ at normalized polymer concentrations of $c/c^* = 0.05, 0.1, 0.3, 0.5, 0.7, 1$, and $2$. To account for the missing glycerol in the PAA stock, additional glycerol was added to ensure that the solvent composition was 80(w/w)% glycerol–water. Suspensions were tumbled for 3 to 5 days to ensure that they were homogenized. Once completely mixed, vials were centrifuged for 3 min at 200g to remove any bubbles before imaging.

We constructed glass chambers for imaging experiments using glass cover slides and UV-curable epoxy (Norland Optical). A microscope glass slide (VWR) was cut into two roughly 20 mm × 15 mm pieces. These pieces were glued onto a 48 mm × 65 mm × 0.15 mm glass coverslip (VWR). To create a chamber, we added a third coverslip (VWR) of dimensions roughly 25 mm × 25 mm × 0.2 mm to the top of the glass slide pieces. Approximately 100 μL of suspension was pipetted into the glass chamber, which was sealed using UV-curable epoxy. We imaged enclosed suspensions roughly 30 min after removal from the horizontal roller.

Confocal Imaging and Tracking Analysis. A Leica DMi8 fluorescence microscope with confocal head series Leica SP8 equipped with a 63X oil-immersion objective was used to image the suspensions. To characterize the 3-D structure of the particles, series of 3-D images were captured at vertical positions from 25 to 65 μm at a step size of 0.1 μm. Ten of these image series were acquired at 13.8 frames per second (fps) at different spatial locations within the chamber. To characterize the particle dynamics, 2-D images were collected as a function of time at a fixed position of 30 μm above the bottom of the coverslip and a frame rate of 9.4 fps for 1000 frames. Ten of these 2-D image series were collected at different locations within the suspension. For 2-D images, a tracking algorithm was used to link the particle centroids into trajectories over time.

We report a static 2-D tracking error of ±39 nm determined from a dilute particle suspension in the absence of polymer to ensure particles are fully diffusive. For 3-D images, the z-locations of the particle centroids were located to submicrometer accuracy.

From the 3-D particle trajectories, we calculate the radial distribution function $g(r)$, contact number (CN), and number density fluctuation $\langle N^2 \rangle - \langle N \rangle^2$, where $N$ is the number of particles in a defined cubic box of length $L$. From the 2-D particle trajectories, we calculate the ensemble-averaged mean-square displacement MSD = $\langle (x(t + \tau) - x(t))^2 \rangle$, self part of the van Hove correlation function $G(x, t) = \frac{1}{N} \sum_{n=1}^{\infty} \delta(x - [x(t) - x(0)])$ and radius of gyration $R_g$ of particle trajectories.

RESULTS AND DISCUSSION

Particle Aggregation Depends on Polymer Size. We previously investigated the effects of pH and PAA polymer concentration on the polymer-bridging-driven aggregation of TtMA particles using confocal microscopy. Prior to the imaging, we measured the effects of molecular weight $M_w$ on the suspension structure and dynamics.

Polymer radius of gyration was calculated from intrinsic viscosity using the two-term virial expansion of viscosity, $\eta = \eta_0(1 + [\eta]C_{PAAM})$, where $[\eta]$ is the intrinsic viscosity, $\eta_0$ is the solvent viscosity, and $C_{PAAM}$ is the polymer concentration, for all PAA molecular weights in 80(w/w)% glycerol–water. Prior to the imaging, we measured the effects of molecular weight $M_w$ on the suspension structure and dynamics.
Figure 1. (a–d) Schematic representation (not to scale) of bridging of TtMA particles (pink) by PAA polymers of molecular weight 130 (a, orange), 450 (b, green), 3000 (c, blue), and 4000 kDa (d, purple). (e–h) Static confocal micrographs of bridging suspensions $\phi = 0.05$ containing PAA of molecular weight 130 (e), 450 (f), 3000 (g), and 4000 kDa (h) at a constant normalized polymer concentration $c/c^* = 0.3$. The brightness and contrast of each micrograph were adjusted for clarity. The scale bars indicate 10 $\mu$m.

Figure 2. (a, d) Radial distribution function $g(r)$ as a function of normalized distance from the particle $r/(2a)$ for PAA molecular weight of (a) 130 and (d) 4000 kDa. (b, e) Probability distribution of contact number for PAA molecular weight of (b) 130 and (e) 4000 kDa. (c, f) Number density fluctuation (NDF) as a function of normalized polymer concentration $c/c^*$ for PAA molecular weight of (c) 130 and (f) 4000 kDa. The particle volume fraction is $\phi = 0.05$ in all suspensions. Symbols indicate the normalized polymer concentration: $c/c^* = 0.05$ (▲), 0.1 (■), 0.3 (▲), 0.5 (▼), 0.7 (◆), 1 (❖), and 2 (●).
work showed that the conformation of the adsorbed polymer depends on the surface coverage and molecular weight, which in turn affects the strength and range of the bridging interactions. Because longer polymers are more likely to be able to extend beyond the range of electrostatic repulsion of the particles, we expect that changing the polymer molecular weight will affect the structure and dynamics of the TiMA suspensions. Based on prior studies, we expect that larger flocks will form as the molecular weight of the polymer is increased. The increase in flock size manifested in both the volume and number of particles in a flock (illustrated schematically in Figure 1a–d).

At a constant normalized polymer concentration of \( \frac{c}{c^*} = 0.3 \), the polymer molecular weight indeed alters the structure of aggregates. Particles bridged by the largest polymers (4000 kDa, Figure 1h) form larger flocks than those bridged by the smallest polymers (130 kDa, Figure 1e). The polymer size also affects the number of free particles. Suspensions containing \( M_w = 130 \) kDa polymers contain free particles as well as small clusters, whereas nearly all particles belong to clusters in suspensions containing \( M_w = 4000 \) kDa polymers. This observation is also consistent with the idea that larger polymers can more readily overcome the electrostatic repulsions between particles. Representative confocal micrographs for the other normalized polymer concentrations are shown in Supporting Information (Figure S1).

**Structure of Suspensions with 130 and 4000 kDa PAA.**

We first examined the effects of PAA \( M_w \) on the structure of TiMA bridging suspensions for normalized polymer concentrations \( \frac{c}{c^*} \) ranging from 0.05 to 2. We present the characterizations of the lowest (130 kDa) and highest (4000 kDa) molecular weights; data for the intermediate \( M_w \) values are provided in the Supporting Information (Figure S2). For suspensions containing a low-\( M_w \) polymer (130 kDa), the radial distribution function \( g(r) \) exhibits a sharp local maximum at interparticle contact \( (r = 2a) \approx 1 \) and a second local maximum at \( r/(2a) \approx 1.8 \) (Figure 2a). The presence of first- and second-neighbor shells is consistent with previous structural measurements on arrested colloidal depletion gels. The height of the first maximum increases concomitant with PAA concentration up until \( \frac{c}{c^*} = 0.3 \). At higher polymer concentrations, the height of the first maximum decreases with addition of PAA, consistent with the decrease in clustering observed in our previous study at high concentrations of PAA. At the highest concentrations of PAA examined \( (\frac{c}{c^*} = 1–2) \), \( g(r) \) approximates a step function with only a weak local maximum. This result is consistent with saturation of the particle surfaces with the polymer such that the polymer acts as a steric stabilizer to generate repulsive interactions.

As a second measure for short-range structure, we calculated the contact number (CN) distribution, using a distance cutoff of \( r/(2a) = 1.6 \) that was determined from the first minimum in \( g(r) \) of the most flocculated suspension (i.e., the suspension that contains the largest clusters) \( (\frac{c}{c^*} = 0.3) \). Increasing \( \frac{c}{c^*} \) leads to pronounced changes in the distributions of CN. For suspensions containing 130 kDa polymer with \( \frac{c}{c^*} \) of 0.05–0.3, the CN distribution exhibits a maximum at \( \approx 4 \), indicating that the most likely number of nearest neighbors is 4 (Figure 2b). The probability of CN \( > 4 \) increases as \( \frac{c}{c^*} \) approaches 0.3. As normalized polymer concentration is increased further \( (\frac{c}{c^*} > 0.3) \), the peak in the CN distributions shifts to lower CN \( \approx 2 \). At \( \frac{c}{c^*} = 2 \), the maximum is located at CN \( \approx 2 \), consistent with a suspension that contains both dispersed particles and small clusters. The evolution in the CN distribution with increasing \( \frac{c}{c^*} \) for low normalized polymer concentrations is consistent with measurements on a silica–PEI (\( \phi = 0.30, M_w = 1200 \)) bridging gel, for which the increase in CN was attributed to the increasing number of particles belonging to the arrested network. At the higher volume fraction, ref 27 did not observe nonmonotonic changes in the microscopic properties with polymer concentration, although the mechanical properties (i.e., elastic modulus) exhibited a local maximum at an intermediate concentration. In our system, however, the nonmonotonic dependence of the CN maximum on \( \frac{c}{c^*} \) likely reflects the steric stabilization (i.e., increasing dispersion) of the particles. Full steric stabilization occurs at \( \frac{c}{c^*} \approx 1.7 \) for this \( M_w \) (Figure S1a); thus, we posit that the decrease in CN above \( \frac{c}{c^*} = 0.5 \) reflects the stabilization of an increasing fraction of particles.

To quantify the cluster structure on longer length scales, we calculate the number density fluctuations (NDF) at a normalized length scale of \( a/L = 0.16 \), in which \( L = 5 \) \( \mu \)m is the bin size (Figure 2c). We select the length scale \( a/L \) as the location of the maximum in NDF(\( L \)) of the strongest gel (\( \frac{c}{c^*} = 0.3 \)) at this \( M_w \), following established protocols. The NDF \( \approx 5 \) at \( \frac{c}{c^*} = 0.05 \) and increases to \( \approx 7 \) for \( \frac{c}{c^*} = 0.3 \), consistent with the formation of clusters of particles (i.e., increasing spatial heterogeneity). As \( \frac{c}{c^*} \) is increased beyond 0.3, however, the NDF decreases and approaches \( \approx 1 \) at the highest normalized polymer concentration \( (\frac{c}{c^*} \approx 2) \), indicating that the particle structure becomes more uniform on this length scale. In this system, the decreases in the most-probable CN combined with the decrease in the NDF suggest that the particles are increasingly dispersed at higher \( \frac{c}{c^*} \). This result is in contrast to the decrease in NDF with increasing polymer concentration observed for the higher-\( \phi \) gels in ref 27, which reflected the increasingly uniform structure of an arrested, elastic gel network.

Increasing the molecular weight of the polymer to 4000 kDa alters the trends in the evolution of structure with increasing polymer concentration. All suspensions containing the 4000 kDa polymer exhibit a pronounced first local maximum in \( g(r) \) (Figure 2d). The height of the first maximum increases with polymer concentration up to \( \frac{c}{c^*} \approx 0.7 \), a higher concentration than for the 130 kDa polymers, and subsequently decreases. At a given \( \frac{c}{c^*} \), the height of this first local maximum is greater than that of the corresponding 130 kDa sample, indicating that the particles exhibit stronger local structural correlations in the presence of the higher-\( M_w \) polymer. The \( g(r) \) for the 4000 kDa samples exhibit both second- and third-local maxima at all concentrations, suggesting that larger clusters form in the presence of a higher-\( M_w \) bridging polymer. As normalized polymer concentration is increased above \( \frac{c}{c^*} = 0.7 \), the heights of all three maxima decrease, indicating that the nearest-neighbor correlations weaken at high normalized polymer concentrations.

The contact number distributions for suspensions containing 4000 kDa polymers exhibit local maxima at higher CN values than those at corresponding \( \frac{c}{c^*} \) values for the 130 kDa polymers (Figure 2e). The value of CN at the maximum is, again, a nonmonotonic function of the normalized polymer concentration, increasing from \( \approx 4 \) at \( \frac{c}{c^*} = 0.05 \) to \( \approx 7–8 \) at \( \frac{c}{c^*} = 0.7 \) and then decreasing to \( \approx 5–6 \) at \( \frac{c}{c^*} = 2 \). The greater CN at the local maximum is consistent with the strong interparticle correlations inferred from \( g(r) \) and the order-of-magnitude greater number of binding sites on this polymer compared to the 130 kDa polymer (Supporting Information Table S1). Likewise, the decrease in CN at higher normalized polymer concentrations is consistent with the
Hove correlation functions of polymer solutions of various molecular weights, showing an initial decrease in the mean-square displacements (MSDs) with normalized polymer concentration. First, we characterized the MSDs in absolute time, noting that the viscosities of charged polymers, the MSDs are subdiffusive (i.e., exhibit a logarithmic slope). The magnitude of the van Hove correlation function $G(\Delta x, \tau)$ as a function of displacement $\Delta x$ at lag times $\tau$ of 0.5 s and 5 s. The particle volume fraction is $\phi = 0.05$ in all suspensions. Symbols indicate the normalized polymer concentration: $c^*/c = 0.05$, 0.1, 0.3, 0.5, 0.8. Gaussian fits to each of the van Hove plots (b, c, e, f) are shown in black.

Dynamics of Suspensions with 130 and 4000 kDa PAA.

We first characterize the mean-square displacements (MSDs) of TtMA particles in bridging suspensions containing 130 and 4000 kDa PAA (data for the other two molecular weights are shown in Figure S3 in the Supporting Information). We report the MSDs in absolute time, noting that the viscosities of charged polymer solutions of various $M_w$ at the same $c^*$ are equal. MSDs corrected for the change in the background viscosity due to the presence of the polymer are shown in Supporting Information (Figure S8). For suspensions containing 130 kDa polymers, the MSDs are subdiffusive (i.e., exhibit a logarithmic slope of less than 1) on short time scales and exhibit approximately diffusive scaling (i.e., exhibit a logarithmic slope close to 1) on long time scales (Figure 3a). The magnitudes of the MSDs on long time scales exhibit weak re-entrance as a function of normalized polymer concentration, first decreasing as $c^*$ increased up to 0.5 and then increasing at higher normalized polymer concentrations such that the fastest diffusion (i.e., greatest MSD) occurs at $c^* = 2$. This trend is consistent with the re-entrant changes in structure as a function of $c^*$ (Figure 3) and thus likely reflects the formation of larger and then smaller clusters with increasing normalized polymer concentration as the surfaces of the particles become saturated by the polymers.

On short time scales ($\tau = 0.5$ s), the shape of the self-part of the van Hove correlation function $G(\Delta x, \tau)$ depends on the polymer concentration. For suspensions with $c^*/c = 0.05$, $G(\Delta x, \tau)$ is non-Gaussian and exhibits pronounced extended tails. Upon further increasing the polymer concentration, the width of the distribution decreases and $G(\Delta x, \tau)$ becomes approximately Gaussian at $c^*/c = 2$. Qualitatively similar nonmonotonic dependence of $G(\Delta x, \tau)$ on $c^*/c$ is observed at a longer lag time $\tau = 5$ s (Figure 3c). For this $\tau$, however, the width of the distribution is greatest at $c^*/c = 0.3$ and decreases with increasing normalized polymer concentration thereafter, with the distribution at $c^*/c = 2$ again approximating a Gaussian. Given that these samples are not dynamically arrested, the strikingly extended tails in the low $c^*$ samples likely indicate distinct populations of mobile and arrested particles.

By contrast, the particle dynamics in suspensions containing a higher molecular weight PAA, $M_w = 4000$ kDa, are nearly arrested at all polymer concentrations. For all $c^*$, the slope of the MSD is nearly zero, consistent with dynamic arrest and hence gel-like behavior on accessible time scales (Figure 3d). The observed near-arrest is consistent with the large $R_g$ observed for suspensions with $M_w = 4000$ kDa (Figure 2d–f), whose formation is driven by the larger $R_g$ of this polymer. On longer time scales, the MSDs for all samples increase slightly and exhibit a nonmonotonic dependence on polymer concentration (as also observed for the 130 kDa samples). The magnitude of...
the MSD first decreases as \( c/c^* \) is increased to 0.7 and subsequently increases upon further addition of polymer up to \( c/c^* = 2 \). The weakly nonmonotonic dependence of the MSD is consistent with the trend in changes in structure with increasing polymer concentration (Figure 2d−f).

For suspensions containing 4000 kDa PAA, the evolution of the van Hove correlation function \( G(\Delta x, \tau) \) with polymer concentration exhibits qualitatively different trends than for the smaller polymer. As for the smaller 130 kDa PAA, \( G(\Delta x, \tau) \) has extended tails at \( c/c^* = 0.05 \) for both \( \tau = 0.05 \) s (Figure 3e) and 5 s (Figure 3f). The width of the distribution, however, decreases monotonically (save for \( c/c^* = 0.5 \) at \( \tau = 5 \) s) as \( c/c^* \) is increased. Similarly extended tails have been observed in bridging \(^{27}\) as well as depletion \(^{37}\) gels and in dynamically arrested systems that are typically attributed to heterogeneous dynamics. Confocal micrographs of this sample (Figure S1), however, show diverse as well as flocculated particles, suggesting that these extended tails may have a different origin than in fully aggregated suspensions.

**Biphasic Behavior at Low \( c/c^* \).** The differences in the width and shape of the van Hove distributions with concentration (Figure 3) and the sample micrographs (Figure S1) suggest that the dynamics may include contributions from distinct populations of particles \(^{27}\) at selected values of \( c/c^* \) and \( M_w \). To identify such biphasic dynamics in our suspensions, we applied a criterion from ref 27 and examined the dependence of the trajectory radius of gyration \( R_g \) on the number of points in the trajectory \( N \).

Figure 4. \((a−c)\) Radius of gyration of particle trajectories \( R_g \) as a function of the number of points in the trajectory \( N \) for suspensions containing PAA of \( M_w \) \((a)\) 4000 kDa at \( c/c^* = 0.05 \), \((b)\) 4000 kDa at \( c/c^* = 0.5 \), and \((c)\) 130 kDa at \( c/c^* = 2 \). The black line in \((a)\) separates the diffusive (above) and arrested (below) populations.

Figure 5. Representative particle trajectories of \((a, d, g, h, j)\) a freely diffusing particle and \((b, e, k, n, p, q)\) an arrested particle for PAA molecular weight of \((a, b, d, e, g, h)\) 130 and \((j, k, m, n, p, q)\) 4000 kDa at \( c/c^* = 0.05 \) \((a, b, j, k), 0.5 \((d, e, m, n), \) and \((2 \((g, h, p, q)\) \((c, f, i, l, o, r)\) 3-D renderings \((\text{thickness } \Delta z \approx 13 \mu m)\) of suspensions with \( \phi = 0.05 \) and \( c/c^* = 0.05 \) \((c, l), 0.5 \((f, o), \) and \(2 \((i, r)\) for PAA \( M_w \) of 130 \((c, f, i)\) and 4000 kDa \((l, o, r)\). Particle color indicates its contact number (CN).
population, for which \( R_g \) is approximately independent of \( N \) (Figure 4a). The diffusive and arrested populations respectively fall above and below the straight line in Figure 4a. We do not observe exchange of particles between clusters and the dispersed phase, likely due to the strength of the multivalent hydrogen bonds between the polymer and the particle stabilizer. The observation of biphasic dynamics in this sample is consistent with the confocal micrographs, which reveal both free and flocculated particles (Supporting Information Figure S1).

Suspensions with 4000 kDa PAA at a concentration of \( c/c^\ast = 0.5 \), however, contain only one population of arrested particles (Figure 4b), whereas suspensions with 130 kDa PAA at a concentration of \( c/c^\ast = 2 \) contain only one population of diffusive particles (for which \( R_g \) increases with \( N \), Figure 4c). Notably, biphasic behavior occurs where distinct populations of disperse and arrested particles form at low \( c/c^\ast \) (for all \( M_w \)), where there is insufficient polymer to bridge all particles, or high \( c/c^\ast \) (for 4000 kDa), where the suspensions contain some sterically stabilized particles alongside particles in clusters. Both observations are consistent with expectations based on confocal microscopy (Supporting Information Figure S1).

Using the dependence of \( R_g \) on \( N \) to identify and distinguish diffusive and arrested particles, we examine the connection between the dynamics and structure of the 130 and 4000 kDa suspensions as a function of \( c/c^\ast \) (Figure 5). Two types of trajectories are observed for suspensions with 130 kDa and \( c/c^\ast = 0.05 \) and 0.5: diffusive (Figure 5a,d) and arrested (Figure 5b,e). 3-D renderings of these samples, meanwhile, also reveal distinct populations of particles with high (clustered) and low (disperse) CN values (Figure 5c.f). These samples thus exhibit biphasic behavior, with distinct populations of disperse and flocculated particles. Increasing the normalized polymer concentration from \( c/c^\ast = 0.05 \) to 0.5 drives a decrease in the population of disperse particles and a concomitant increase in flocculation (i.e., in particles with higher CN). At \( c/c^\ast = 2 \), however, the trajectories are approximately diffusive and particles are largely disperse (Figure 5i). These results suggest that the particles are fully stabilized by 130 kDa polymer at high concentrations.

Biphasic behavior is less pronounced upon increasing the polymer \( M_w \) to 4000 kDa, consistent with the enhanced flocculation observed in these samples. Suspensions with \( c/c^\ast = 0.05 \) exhibit biphasic behavior, as indicated by two types of trajectories and by the observation of flocculated and disperse particles in 3-D renderings reconstructed from z-stack particle positions (Figure 5j–l). Increasing the normalized polymer concentration to \( c/c^\ast = 0.5 \) drives the formation of large clusters in which all particles have many nearest neighbors, and particles primarily exhibit arrested trajectories (Figure 5m–o). Finally, suspensions with \( c/c^\ast = 2 \) form looser clusters, as indicated by the slightly lower CN values compared to \( c/c^\ast = 0.5 \), and the particle trajectories are mostly arrested (Figure 5p–r). Thus, the polymer size affects the propensity of suspensions to form biphasic mixtures.

**State Diagram for Bridging Suspensions.** We summarize the data on bridging suspensions formulated with polymers of different \( M_w \) and \( c/c^\ast \) on a state diagram. As a metric, we examine the NDF as a function of the \( c/c^\ast \) and \( M_w \) (Figure 6). For each polymer \( M_w \), the NDF first increases and then decreases as a function of normalized polymer concentration. The range of NDF values and the value of \( c/c^\ast \) at which the NDF attains its maximum are distinct for the low (130, 450 kDa) and high (3000, 4000 kDa) \( M_w \) polymers. For suspensions containing 130 and 450 kDa polymers, the NDF values range from \( \approx 1 \) to \( \approx 9 \), and the maximum NDF occurs at \( c/c^\ast \approx 0.3 \). For suspensions containing 3000 and 4000 kDa polymers, the NDF values range from \( \approx 5 \) to \( \approx 12 \), indicating that larger polymers lead to suspensions with greater structural heterogeneity. Further, the maximum NDF for these suspensions occurs at a slightly higher value, \( c/c^\ast \approx 0.5 \). At a constant \( c/c^\ast \) (i.e., approximately constant background viscosity), the structures become more heterogeneous (larger NDF) as the \( M_w \) is increased.

### CONCLUSION

We show that polymer molecular weight \( M_w \) markedly alters the structure and dynamics of a bridging system consisting of TtMA copolymer particles and adsorbing PAA of molecular weights 130, 450, 3000, and 4000 kDa. Suspensions containing 130 kDa PAA remain fluid-like across the range of normalized polymer concentrations investigated (\( c/c^\ast = 0.05 \sim 2 \)) and exhibit local maxima in structural metrics (i.e., contact number and local structure) and slowest dynamics at a normalized concentration \( c/c^\ast \approx 0.5 \). The fluidization of these samples upon further increase in polymer concentration is due to steric stabilization of a growing fraction of the particles as the particle surfaces become saturated with polymer. Suspensions containing 4000 kDa PAA exhibit arrested dynamics and larger clusters than at 130 kDa, with similar nonmonotonic dependence of properties occurring at normalized concentrations \( c/c^\ast > 0.7 \). For both \( M_w \), the onset of nonmonotonic behavior occurs at \( c/c^\ast \) values below those required for full steric stabilization of the particles, indicating that some particles become sterically stabilized even at modest \( c/c^\ast \). Biphasic behavior, reflecting distinct populations of freely diffusing and flocculated arrested particles, is observed at \( c/c^\ast \approx 0.5 \) for both \( M_w \).

Our results confirm that the polymer \( M_w \) alters the size of flocs, as found in earlier studies, and the microscopic dynamics. The methods employed here may prove useful to elucidate size effects of other types of bridging agents, such as microgel particles, and other types of particles, such as emulsions, on particle structure and dynamics. Further, the biphasic behavior occurring at selected \( M_w \) and \( c/c^\ast \) may offer an alternative route to obtaining favorable combinations of rheological properties for extrusion-based processes such as 3-D printing. We anticipate that studies in this system of the bulk
rheological properties will provide guidance toward formulating flowable, low-clogging particulate suspensions for these applications. Finally, we anticipate that similar studies in suspensions with variable particle size will enable a zoo of rheological behaviors, including shake gels and rheoprecipitate and thixotropic fluids to be connected to microscopic interactions.

ASSOCIATED CONTENT

Supporting Information

Confocal micrographs of all suspensions (Figure S1), structure of 450 and 3000 kDa (Figure S2), dynamics of 450 and 3000 kDa (Figure S3), radius of gyration as a function of frames for 3000 kDa (Figure S4), particle trajectories and 3-D renderings of 450 and 3000 kDa (Figure S5), radial distribution function with error bars for all suspensions (Figure S6), mean squared displacements with error bars for all suspensions (Figure S7), MSDs as a function of a rescaled time to account for changes in background viscosity (Figure S8), shifted $g(r)$ for clarity (Figure S9), critical polymer concentration for surface saturation (Figure S10), state diagrams as a function of $R_g^2/R_{\text{particle}}$ (a) and maximum CN (b) (Figure S11), Yukawa potential of TtMA particles (Figure S12), and available binding sites for all PAA molecular weights and $c/c^*$ (Table S1) (PDF)

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Notes

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