

# Soft Interactions Modify the Diffusive Dynamics of Polymer-Grafted Nanoparticles in Solutions of Free Polymer

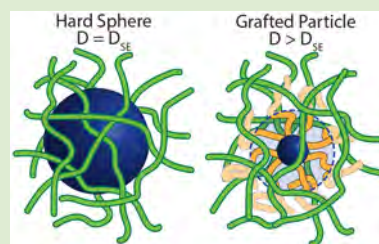
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## S Supporting Information

**ABSTRACT:** We examine the dynamics of silica particles grafted with high molecular weight polystyrene suspended in semidilute solutions of chemically similar linear polymer using X-ray photon correlation spectroscopy. The particle dynamics decouple from the bulk viscosity despite their large hydrodynamic size and instead experience an effective viscosity that depends on the molecular weight of the free polymer chains. Unlike for hard-sphere nanoparticles in semidilute polymer solutions, the diffusivities of the polymer-grafted nanoparticles do not collapse onto a master curve solely as a function of normalized length scales. Instead, the diffusivities can be collapsed across two orders of magnitude in free polymer molecular weight and concentration and one order of magnitude in grafted molecular weight by incorporating the ratio of free to grafted polymer molecular weights. These results suggest that the soft interaction potential between polymer-grafted nanoparticles and free polymer allows polymer-grafted nanoparticles to diffuse faster than predicted based on bulk rheology and modifies the coupling between grafted particle dynamics and the relaxations of the surrounding free polymer.



Attaching polymers to surfaces modifies the interactions between nanoparticles and the surrounding environments. Such fine-tuning of nanoparticle interactions is important to improve the biocompatibility of targeted drug delivery vectors,<sup>1–4</sup> control self-assembled structures in nanocomposites,<sup>5–8</sup> or stabilize emulsions.<sup>9–11</sup> For these applications, the efficacy of polymer-grafted nanoparticles (PGNPs) requires that the particles remain stable and transport effectively when dispersed into complex fluids. Whereas the long-time dynamics of large hard-sphere colloids through complex fluids are well understood, multiple factors complicate predictions of the motion of PGNPs. First, PGNPs are often comparably sized to heterogeneities in complex fluids, violating an assumption underlying microrheology theory.<sup>12–14</sup> Second, PGNPs are soft particles whose “softness” can be characterized by their elastic deformability<sup>15</sup> or through the steepness and range of their repulsive interactions.<sup>16–18</sup> The combination of soft interactions between grafted polymers and hard interactions of the nanoparticle cores leads to elastic moduli and yield stresses for PGNP suspensions lower than those of hard-sphere colloids and higher than those of “ultra-soft” star-like polymers or micelles.<sup>16,19,20</sup> Finally, tethering of polymer to the particle surface significantly changes the grafted polymer relaxations<sup>21–24</sup> and may therefore affect the transport of PGNPs.

Here, we investigate the dynamics of silica nanoparticles grafted with high molecular weight polystyrene so that the grafted polymer and silica core are comparably sized. The PGNPs are dispersed into solutions of free polystyrene, and the dynamics of the PGNP center-of-mass are probed using X-

ray photon correlation spectroscopy (XPCS). The PGNP dynamics systematically depend on the free polymer molecular weight so that PGNPs diffuse faster in solutions with the same bulk viscosity but higher molecular weight. Although similar dependences have been observed for hard-sphere nanoparticles, the PGNPs are much larger than the length scale at which hard spheres decouple from bulk viscosity, and the PGNP diffusivity does not collapse according to relative size as it does for hard spheres. We propose that these unique transport properties of PGNPs arise from the soft interaction between the PGNP corona and the free chains in solution.

We graft<sup>24</sup> polystyrene with molecular weight  $M_{w,g} = 33$  and 355 kDa onto silica nanoparticles of radius  $R = 24$  nm to form PGNPs with a morphology intermediate between a pseudo-hard sphere (low grafted  $M_w$ ) and a star polymer (high grafted  $M_w$ ). Respectively, the 33 and 355 kDa PGNPs have grafting densities  $\sigma = 0.08 \pm 0.01$  chains  $\text{nm}^{-2}$  ( $580 \pm 70$  chains per particle) and  $0.06 \pm 0.015$  chains  $\text{nm}^{-2}$  ( $430 \pm 90$  chains per particle) determined from thermal gravimetric analysis, hydrodynamic radii  $R_H = 70$  and 110 nm determined from dynamic light scattering, and overlap concentrations  $c_{\text{PGNP}}^* = 0.11$  and  $0.023$   $\text{g mL}^{-1}$  determined from intrinsic viscosity. Small-angle neutron scattering (SANS) experiments are conducted on the NG7 30m beamline<sup>25,26</sup> at the NIST Center for Neutron Research on PGNPs dispersed in partially deuterated  $d_5$ -2-butanone and partially deuterated

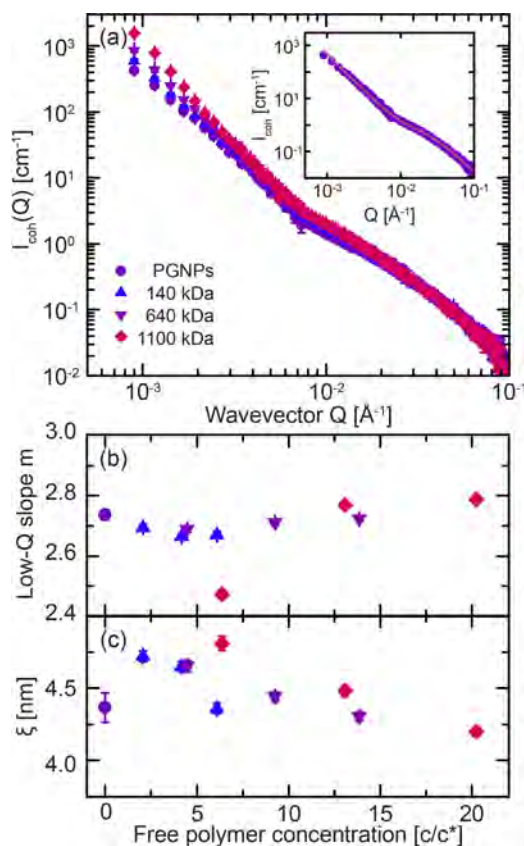
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$d_3$ -polystyrene with  $M_w = 140, 640,$  and  $1100$  kDa to contrast-match the silica core. XPCS measurements were conducted on the 8-ID-I beamline at Argonne National Lab on PGNPs dispersed in protonated solvent and polystyrene with  $M_w = 150, 590, 1100,$  and  $15000$  kDa, which span the molecular weight of the grafted chain over a range that controls PGNP dispersion in polymer melts.<sup>7</sup> PGNPs remained well dispersed in all solutions (Supporting Information). Steady-shear rheology experiments on protonated solutions were conducted on a Discovery Hybrid Rheometer (TA Instruments, HR-2) using a Couette geometry.

Previous experiments<sup>27,28</sup> and simulations<sup>29,30</sup> have identified rich structural changes for PGNPs dispersed in solutions of free chains. We first investigate using SANS the structure of 355 kDa PGNPs dispersed in partially deuterated solutions to isolate scattering from the grafted polymer (Figure 1). At large



**Figure 1.** (a) Coherent SANS intensity  $I_{\text{coh}}$  as a function of wavevector  $Q$  for 355 kDa PGNPs dispersed at  $\approx 1c_{\text{PGNP}}^*$  in solutions of  $d_5$ -2-butanone and free  $d_3$ -polystyrene of various  $M_w$  at  $c = 0.15$  g mL<sup>-1</sup>. Inset:  $I_{\text{coh}}(Q)$  for PGNPs with no free polymer. Solid curve is best fit to eq 1. (b) Low- $Q$  slope  $m$  and (c) correlation length  $\xi$  as a function of free polymer concentration.

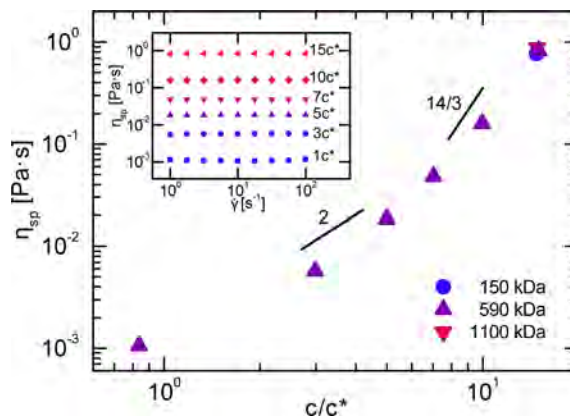
$Q$ , the intensity derives from intra- and interchain correlations, whereas at low  $Q$ , the scaling of the intensity corresponds to the sharpness of the interface between the PGNP corona and surrounding solvent. Because these PGNPs are large, we do not observe a low- $Q$  plateau and thus cannot model the scattering intensity using existing models derived for grafted morphologies.<sup>31–34</sup> Instead, we model the full scattering intensity as the sum of a Lorentzian to capture the polymer conformation inside the corona and a power law to model the sharpness of the corona–solvent interface according to

$$I_{\text{coh}}(Q) = \frac{I_{\text{poly}}}{1 + (Q\xi)^{1/\nu}} + AQ^{-m} \quad (1)$$

where  $I_{\text{poly}}$  is corona polymer intensity;  $\xi$  is the correlation length between grafted chains;  $\nu$  is the excluded volume parameter; and  $m$  is the low- $Q$  slope. Because the amount of grafted polymer does not change in these solutions, we hold  $I_{\text{poly}}$  constant and let the other parameters float.

Physically, grafted brushes are expected to compress in solutions of free chains.<sup>24,27,28,35</sup> Changes in the scattering pattern as the concentration and molecular weight of free polymer vary are consistent with this physical picture. When polymer is first added to the system,  $m$  decreases and  $\xi$  increases (Figure 1(b,c)). These changes could be caused by a small expansion of the grafted corona. Upon increasing free polymer concentration,  $m$  decreases in solutions with low concentrations of low  $M_w$  free polymer but increases in more concentrated solutions of higher  $M_w$ . This dependence suggests that the boundary between the grafted corona and surrounding solution becomes slightly more diffuse at low concentrations and sharper at higher concentrations. Inside the grafted corona,  $\xi$  decreases with increasing free polymer concentration as the corona compresses and decreases more strongly in solutions with lower molecular weight. This compression is caused by an increase in the solution osmotic pressure by the free chains and a logarithmic interaction potential between free chains and PGNPs<sup>29,30,36</sup> that is softer than the power-law interactions between hard-sphere colloids and polymers in solution.<sup>37–39</sup>

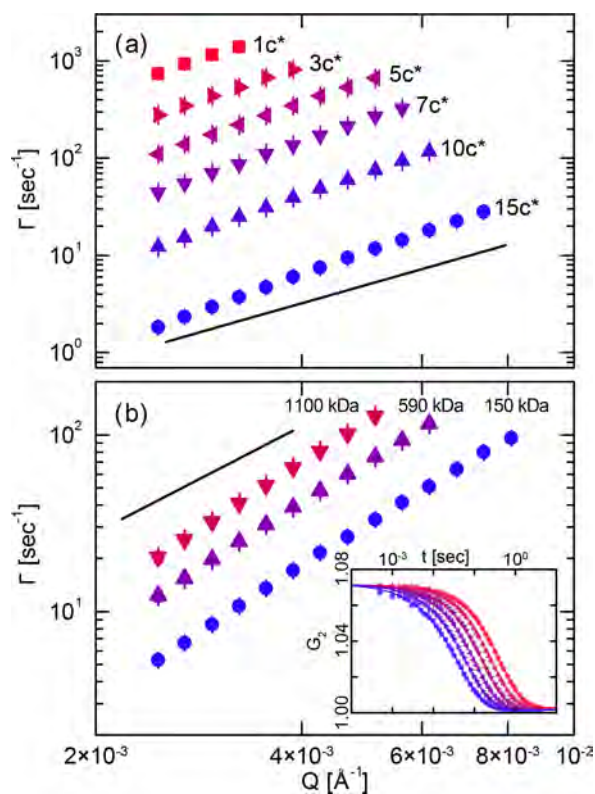
After determining that the structure of the PGNPs agrees with previous studies, we investigate whether the low PGNP concentration modifies bulk solution properties. For polymer solutions, bulk viscosity  $\eta$  scales with relative concentration  $c/c^*$ , independent of  $M_w$ . To verify that this scaling collapse holds for solutions containing free polymer as well as PGNPs, we measure the steady shear viscosity as a function of shear rate  $\dot{\gamma}$ , free polymer concentration, and free polymer molecular weight (Figure 2). The viscosity is Newtonian with relaxation times  $\lesssim 1$  ms (inset to Figure 2) and scales as predicted with  $\eta \sim (c/c^*)^2$  when unentangled and as  $\eta \sim (c/c^*)^{14/3}$  when entanglements dominate.<sup>40</sup> Moreover, the measured viscosities of  $15c^*$  solutions exhibit no significant changes as a function of  $M_w$ . These rheological characteristics are in excellent agree-



**Figure 2.** Specific viscosity  $\eta_{\text{sp}} = \eta - \eta_0$  as a function of free polystyrene concentration  $c/c^*$  for solutions of varying molecular weight. Inset: Specific viscosity  $\eta_{\text{sp}}$  for 590 kDa solutions as a function of shear rate  $\dot{\gamma}$ . All samples contain  $0.5c_{\text{PGNP}}^*$  of 355 kDa PGNPs.

ment with theory for solutions of free polymers, indicating that PGNPs do not perturb the bulk solution rheology.

Having confirmed that the structure and solution rheology follow the expected behavior, we investigate the dynamics of PGNPs in polymer solutions using XPCS. Because the X-ray scattering is dominated by the contrast between the inorganic silica core and the organic solution, the measured dynamics represent only those of the center-of-mass of the PGNP and do not directly reflect the relaxations of the grafted brushes. The intensity autocorrelation curves  $G_2$  decay faster with time at smaller wavevectors  $Q$  and are well fit by  $G_2(Q, \Delta t) = 1 + BG_1(Q, \Delta t)^2 + \varepsilon$  where  $B$  is the Siegert factor that depends on experimental geometry;  $G_1(Q, \Delta t) = \exp[-(\Gamma \Delta t)^\beta]$  is the field correlation function;  $\beta \approx 0.85$  is a stretching exponent that arises from the polydisperse size of the PGNPs; and  $\varepsilon$  captures any residual noise (inset to Figure 3). The relaxation rate

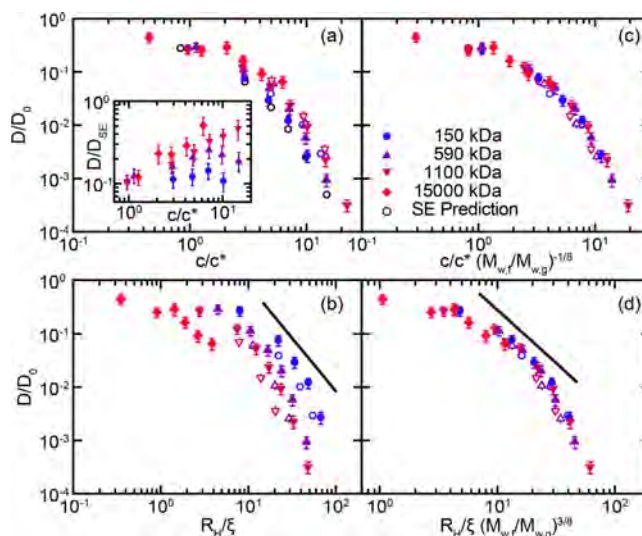


**Figure 3.** Relaxation rate  $\Gamma$  for 355 kDa PGNPs from XPCS as a function of wavevector  $Q$  at (a) various concentrations of 590 kDa free polystyrene and at (b)  $c/c^* = 10$  for  $M_w = 150, 590,$  and  $1100$  kDa. All samples have a PGNP concentration of  $0.5c_{\text{PGNP}}^*$ . Solid lines indicate  $Q^2$  scaling. Inset: Intensity autocorrelation function  $G_2$  as a function of lag time for  $0.003 \text{ \AA}^{-1}$  (red)  $\leq Q \leq 0.0074 \text{ \AA}^{-1}$  (blue) for a solution of  $c/c^* = 23$  and  $M_w = 1100$  kDa. Solid curves are stretched exponential fits.

follows  $\Gamma = DQ^2$ , where  $D$  is the PGNP diffusivity (Figure 3). Because the free polymer increases the bulk solution viscosity, the particle dynamics slow with increasing  $c/c^*$ . Surprisingly, there is an additional dependence on free polymer  $M_w$ : PGNPs diffuse more slowly in solutions of low  $M_w$  than in solutions of high  $M_w$  at the same  $c/c^*$  (Figure 2). This  $M_w$  dependence indicates that the nanoscale dynamics are fundamentally different from those on the macroscale.

To quantify this difference between the nanoscale dynamics of PGNPs and microrheological predictions based on bulk

viscosity, we analyze how the PGNP diffusivity changes with free polymer concentration and molecular weight (Figure 4(a)). Specifically, we compare the measured PGNP diffusivity



**Figure 4.** Normalized PGNP diffusivity  $D/D_0$  as a function of (a) free polymer concentration  $c/c^*$ , (b) ratio of PGNP size and correlation length  $R_H/\xi$ , and  $M_w$ -modified (c) concentration and (d) length scale ratio. Open and closed symbols correspond to  $M_{w,g} = 33$  and  $355$  kDa, respectively. Inset: Diffusivity normalized to SE predictions  $D/D_{\text{SE}}$  as a function of  $c/c^*$ . Solid lines represent predicted scaling of  $-2$  for hard spheres.<sup>42</sup> All samples have a PGNP concentration of  $0.5c_{\text{PGNP}}^*$ .

to predictions based on bulk viscosity  $\eta$  using the Stokes–Einstein (SE) expression  $D_{\text{SE}} = k_B T / 6\pi\eta R_H$ . For  $c/c^* \approx 1$ ,  $D/D_{\text{SE}} \approx 1$  for all free polymer molecular weights. As  $c/c^*$  increases,  $D/D_{\text{SE}} \approx 1$  in the 150 kDa solutions but increases with increasing  $c/c^*$  and  $M_w$  (inset to Figure 4(a)). Although the PGNPs compress in solutions, this compression cannot explain the observed discrepancy in  $D/D_{\text{SE}}$ . According to SANS (Figure 1) and theoretical predictions<sup>41</sup> (Supporting Information), the PGNPs in low  $M_w$  solutions shrink more and should therefore diffuse faster. The observed behavior is exactly opposite: PGNPs diffuse faster at high  $M_w$ . Instead, the discrepancy in  $D/D_{\text{SE}}$  must originate from interactions between PGNPs and the surrounding polymer solution on the nano- or microscale.

The dynamics of large colloidal particles through complex fluids are excellently described in the microrheological framework by the SE or generalized SE expressions.<sup>12–14</sup> Nanoparticles, however, often diffuse faster than expected because they are comparably sized to the polymer coils in solution.<sup>42</sup> For these PGNPs, however, the hydrodynamic radius  $R_H$  is much larger than the polymer radius of gyration  $R_g = 13, 27,$  and  $38$  nm for  $M_w = 150, 590,$  and  $1100$  kDa, respectively.<sup>43</sup> Based on the relative size of the PGNPs it is surprising to observe the  $M_w$  dependence shown in Figure 4(a). A recent coupling theory attempts to explain the enhanced diffusion of hard-sphere nanoparticles in semidilute polymer solutions. Assuming that particle dynamics couple to the segmental relaxations of the surrounding polymer until the polymer relaxes over the particle surface, coupling theory estimates particle diffusivity through a length scale ratio  $D/D_0 \sim (R_H/\xi)^{-2}$ , where  $D_0$  is the nanoparticle diffusivity in solvent.<sup>42</sup> This theory collapses diffusivities of hard-sphere

nanoparticles measured experimentally<sup>44</sup> and in simulations<sup>45</sup> but cannot collapse the PGNP dynamics (Figure 4(b)). The significant difference between the dynamics of PGNPs in solutions with varying  $M_w$  indicates that PGNPs experience local heterogeneities in semidilute polymer solutions differently than hard-sphere particles do.

The ratio between free and grafted polymer  $M_w$  has been shown to control the morphology of PGNPs<sup>5,7</sup> and star polymers<sup>28</sup> in polymer melts and solutions. To determine if this ratio also affects dynamics, we plot the PGNP diffusivity as a function of  $c/c^*$  and  $R_H/\xi$  modified by the ratio of free to grafted polymer molecular weights  $M_{w,f}/M_{w,g}$  (Figure 4(c,d)). Incorporating the  $M_w$  ratio cleanly collapses the PGNP diffusivities across two orders of magnitude in both  $c/c^*$  and free polymer  $M_{w,f}$  and an order of magnitude in grafted polymer  $M_{w,g}$ . In these collapses, the molecular weight scaling exponents are empirically determined to minimize spread in the data. The inverse scaling of  $(M_{w,f}/M_{w,g})^{-1/8}$  required to collapse diffusivity as a function of  $c/c^*$  indicates that the PGNPs experience a lower effective viscosity in solutions of higher  $M_{w,f}$ . By contrast, the collapse according to  $R_H/\xi$  requires a proportional scaling with  $(M_{w,f}/M_{w,g})^{3/8}$  to offset the overcorrection from the hard-sphere scaling. Although the numerical exponents may vary with grafting density or core size, the collapse indicates that the  $M_w$  ratio controls the nanoscale interactions that affect PGNP dynamics in polymer solutions.

Beyond the importance of the  $M_w$  ratio, the PGNP diffusivity also has a different functional dependence on  $R_H/\xi$  than hard spheres. Over a limited range, PGNP diffusivity decreases similarly to theoretical predictions for hard spheres. At higher concentrations, however, PGNP diffusivity decreases more sharply than predicted, suggesting that the dynamics of PGNPs are slowed by entanglements between free polymers. Such entanglement-controlled dynamics are not observed for hard-sphere nanoparticles until the particle radius exceeds the tube diameter in the entangled solution.<sup>42,46</sup> Although entanglements between star polymer arms and free chains can significantly alter the diffusion of the star core, predictions based on this theory<sup>47</sup> cannot explain the  $M_w$  dependence observed here (Supporting Information). Thus, the diffusive dynamics of PGNPs through polymer solutions cannot be described through theories derived purely for hard-sphere nanoparticles or star polymers.

To guide future investigations, we consider a variety of physical phenomena that may control how the dynamics of PGNPs differ from those of hard spheres or star polymers. First, compression of PGNPs in solution cannot explain the observed dynamic phenomenon and may not follow star polymer predictions due to the finite size of the core. Complementary characterizations of PGNP dynamics and structure on long length scales are essential. Second, interactions between free and grafted chains can affect the grafted polymer dynamics<sup>24</sup> or the hydrodynamic drag on the PGNP surface.<sup>48,49</sup> Third, the deformability and dynamic relaxations of the grafted polymer may modify how PGNPs couple to segmental relaxations of the free polymer mesh and thus affect transport properties.<sup>42,50</sup> Many or all of these phenomena may play an important role in controlling PGNP diffusion and transport through semidilute polymer solutions, but fundamentally they all derive from soft interaction profiles. These soft interactions introduced by the grafted polymer

result in unexpected dynamic behavior and prevent PGNPs from being treated simply as hard spheres or star polymers.

We investigate the dynamics of nanoparticles grafted with long polymer chains dispersed in solutions of free polymer. Although the PGNPs are much larger than the free polymer chains, their dynamics decouple from bulk solution viscosity in solutions of high molecular weight free polymer, diffusing up to five times faster than expected. Additionally, the PGNP dynamics depend on free polymer molecular weight and do not collapse according to predictions for hard spheres. This lack of collapse suggests that the PGNPs experience local heterogeneities and couple to relaxations in the surrounding fluid differently than hard spheres. We posit that these differences between PGNPs and hard spheres arise due to the soft interaction potential between the grafted corona and the free polymer. Many parameters—including core size, grafted polymer molecular weight, and grafting density—control the physical structure, organization,<sup>5</sup> and interaction potential<sup>51</sup> of PGNPs. Understanding how these parameters modify transport properties is essential to controlling the efficacy of PGNPs dispersed in complex fluids.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.9b00294.

SAXS curves, calculations of PGNP compression, and estimates of arm retraction dynamics (PDF)

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### Notes

The authors declare no competing financial interest.

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