Revisiting Polymer–Particle Interaction in PEO Solutions

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ABSTRACT: We have measured the electrophoretic mobility and diffusion coefficient of carboxylate-modified and sulfate-modified polystyrene latex particles in poly(ethylene oxide) aqueous solutions. Carboxylate-modified polystyrene particles have shown a bound polymeric layer as the surface net charge vanishes even at very low poly(ethylene oxide) concentration. The polymeric layer causes a lower electrophoretic mobility and slower Brownian motion than that corresponding to the bare particles. We show that the diffusion is the result of a significantly increased effective particle size $2\Delta r_{\text{eff}} = 30$ nm. This bound layer is not present in sulfate-modified polystyrene latex particles. The interaction between the carboxylate-modified particle surface and the macromolecules has been confirmed by means of atomistic computer simulations. The grafted acrylate copolymers, which come from the preparation procedure of the latex particles, confer more hydrophobic surface ready to interact with the polymer. The simulations suggest that the interaction is modulated not only by the nature of the acrylic acid monomer but also by the length of the grafted copolymer. Our results have important implications for particle selection in microrheology experiments.

INTRODUCTION

The study of the diffusion of biomacromolecules and micro- or nanoparticles in polymeric media (solutions or in the molten state) has not only basic implications, but also a great interest from the point of view of industrial, medical, and biotechnological applications.1,2 In this context, the development of microrheological techniques has been a great advance, when applied to systems such as polymeric solutions, polymers in the molten state, gels, and biological systems.3–6

In the case of active microrheology, the force exerted on the probe particles is external (magnetic and laser tweezers). The specific case of passive microrheological techniques are based on the monitoring of the Brownian motion of spherical particles, in order to relate this motion with the viscoelastic characteristics of the surrounding medium, by generalizing the well-known Stokes–Einstein relation.7 A challenge in passive microrheology using probes is the design of particles with specific surface properties, in order to avoid interactions with the host medium. Polymeric particles in particular, are especially interesting mainly due to their versatility, tunable sizes, physical properties and low toxicity. The interfacial phenomena on the surface with the local environment may already alter the particle transport in complex media such as polymeric or biological fluids. Also, the size of the probe is important, and, in order to extract the correct viscoelastic fingerprint of the medium, it must be larger than the radius of gyration, $r_g$, of the polymeric chain.8 Interestingly, the use of particles with a size lower than the correlation length might give access to the local properties of the system.9 Notwithstanding, it should be noted at this respect that the question of the probe size effect in microrheology is still open, but it may be exploited to extract interesting features of complex systems at the local scale.

Within all the broad literature studies concerning micro-rheological approaches to study complex systems, we have selected those performed in poly(ethylene oxide) (PEO) aqueous solutions, as they have been used as models for the development of passive microrheological techniques based on diffusing wave spectroscopy (DWS) and dynamic light scattering (DLS). It should be noted that the tracer diffusion of micro- and nanosized particles in polymeric solutions has attracted a great deal of attention from the experimental point of view since the 80s.10–14 Most of these works are focused on the determination of the diffusion coefficient, $D$, of tracer particles of radius $r$ in polymeric solutions, the subsequent application of the Stokes–Einstein relation $D = \frac{k_B T}{6\pi \eta r}$ to obtain the viscosity of the medium, $\eta$, for the subsequent comparison to that measured by mechanical rheology, in most of the cases. The early studies of Phillips et al. in the 80s were...
performed by determining the diffusion coefficient of carboxylated polystyrene latex particles in PEO solutions (among other polymers). In these works, the authors already determined the existence of the “overlapping” and “entangled” regimes as PEO concentration increases, but they also reported the failure of the Stokes–Einstein relationship and the appearance of fast modes in the light scattering spectrum in solutions prepared with the highest molecular weight PEO samples. Remarkably, the authors were able to interpret the measured diffusion coefficients in terms of non-Stokes–Einstein hydrodynamics and the adsorption of the polymeric chains by the optical probes.

In the 90s, Mason and Weitz presented their generalization of the Stokes–Einstein relationship to viscoelastic fluids. These authors used a generalized Langevin equation to relate the measured angular displacement of the probe, \( \langle r^2(t) \rangle \), obtained by light scattering, to the complex modulus of the fluid, \( G^*(\omega) \), in an experimental framework applied to various systems including a specific PEO/water solution and polystyrene latex particles. Since the year 2000, various works have been focused in PEO/water solutions in order to check the validity of the microhydrodynamics, using both carboxylate-modified and sulfate polystyrene latex probes of different sizes. In these works, the effect of surface chemistry is studied indirectly, by comparing the values of \( \langle r^2(t) \rangle \) obtained for a given PEO solution, usually in the entangled regime, using probes with the same chemistry and different sizes (around 0.3 and 2 μm), and comparing the results with those obtained by mechanical rheology. The agreement between the microhydrodynamical and mechanical results was not always exact, and it could be subject of discussion. Zanten et al. studied aqueous PEO solutions using sulfate polystyrene particles in a broader range of concentrations, covering the unentangled and entangled regimes. These authors also determine the absence of particle–polymer interactions and the minimal influence of longitudinal modes in the Brownian motion by using particles of sizes between 0.2 and 2 μm.

It is clear that the main challenge for an efficient use of micro rheological techniques lies on the ability to choose suitable particles to probe the rheological response, that is, those minimizing the particle-sample interaction. The use of more than one particle of the same nature and different sizes is also a quite robust approach, as the mutual fluctuations of both types of probe particles provide an accurate method to determine not only the viscoelastic properties of the suspending medium, but also to study the boundary conditions of the particle/matrix system and inertial effects. Another appropriate property to detect the interaction between particles and surrounding macromolecules is the electrostatic mobility. If the surface properties of the particles are already altered by adsorbed macromolecules to the surface, this property will substantially change. In this work, we have selected sulfate and carboxylate-modified polystyrene latex particles in order to study their suitability to micro rheological studies in PEO/water solutions. We have combined both experiments (electrohydrodynamic mobility and light scattering) and computer atomistic simulations of the systems in order to determine the nature of the particles/polymer interactions.

### Materials and Methods

**Materials and Characterization.** The poly(ethylene oxide) (PEO) sample of \( M_w \sim 300 \text{ kg mol}^{-1} \) was obtained from Sigma-Aldrich. Dust-free PEO aqueous solutions (\( c < 1.5 \text{ mg mL}^{-1} \)) were prepared with deionized water that had been filtered through 0.02 μm syringe filters (Whatman-Anotop 25). The weight-average molecular weight, \( M_w \), and the second virial coefficient, \( B_{20} \), of the PEO sample were determined by static light scattering (SLS) using the Zetasizer Nano ZS apparatus. The measurements for different sample concentrations in the dilute regime were obtained at \( T = 298 \text{ K} \). In addition to the SLS measurements, dynamic light scattering (DLS) experiments and cumulant analysis have been performed at each concentration using the same apparatus, in order to estimate the diffusion coefficient, \( D_0 \), and the hydrodynamic size, \( r_h \), of the polymer coils. In both types of experiments polystyrene cuvettes (Malvern Instruments DTS0012) have been used.

Polystyrene (PS) latex spheres bearing sulfate surface groups (PS-SO4) of nominal radius 30 and 100 nm and carbonyl surface groups (PS-CO2) of nominal radius of 150 nm were utilized as optical probes (Duke Scientific, Palo Alto, CA). The optical probes at 0.1–0.01% v/v were dispersed in water and in solutions with variable concentration of PEO (\( c < 1.0 \text{ mg mL}^{-1} \)) for DLS and electrohydrodynamic mobility (EM) measurements at \( T = 298 \text{ K} \). EM was measured also in the Zetasizer Nano ZS apparatus, which uses phase analysis light scattering (PALS). The universal dip cell with palladium electrodes (Malvern Instruments ZEN1002) were used to perform the measurements. Charged particles are attracted to the oppositely charged electrode, and their velocity was measured and expressed per unit field strength as the EM, \( \mu_r \). The measured conductivity of the solutions remains nearly constant and low, around 0.053 ± 0.017 mS/cm.

The molecular, hydrodynamic, and electrostatic properties obtained at \( T = 298 \text{ K} \) for the nanoparticles and the PEO sample under study are listed in Table 1. The specific details of the experimental procedures and materials characterization can be found in the Supporting Information (SI).

| Table 1. Hydrodynamic and Electrostatic Properties of the Systems under Study at \( T = 298 \text{ K} \) |
|---------------------------------------------|
| sample | \( D \text{ μm}^2 \text{s}^{-1} \) (z- average) | \( r_h \text{ (nm) (z- average)} \) |  | \( Q \) | \( \mu_r \text{ μm cm}^{-1} \text{ V}^{-1} \text{s}^{-2} \) |
| PEO300 | 8.55 | 287 (41.6) | 0.37 | \( -0.52 \pm 0.02 \) |
| PS-SO4 | 7.00 | 35.0 | 0.03 | \( -3.2 \pm 0.2 \) |
| PS-SO4 | 8.38 | 101.0 | 0.03 | \( -3.8 \pm 0.2 \) |
| PS-CO2 | 1.66 | 148.0 | 0.03 | \( -3.6 \pm 0.1 \) |

**Computer Simulations.** The atomistic structure of the surface of the nanoparticles has been constructed by taking into account the specific features of the real systems (see point 3 of the SI). The large size of the nanoparticle (35–148 nm of radius) and the high molecular weight of the polymer (284.1 kg mol\(^{-1}\)) make impractical the atomistic simulations of these systems. For this reason, the atomistic models have been built on a small-scale model able to capture the interactions between the surface of the nanoparticle and the polymer solution. Thus, a central bilayer model representing a small fraction of the nanoparticle surface was built resulting in two interacting sides each mimicking the nanoparticle surface.

In order to assess the effect of the different surfactant/polymer models on the bilayer-polymer interactions, the following simulation systems were built (see SI Scheme S1): (1) A slab containing 64 polystyrene (PS) oligomers composed of 10 monomeric units, each capped at both ends with SO4\(^-\) groups, was built as an 8 × 8 × 8 layer at the center of a simulation box. The system is intended to mimic a surfactant free sulfonated nanoparticle surface (PS-SDS-free). (2) A bilayer of SDS molecules where either 4 (PS-4-SDS) or 9 (PS-9-SDS) PS oligomers are inserted at regular positions mimicking a surfactant saturated nanoparticle surface. The SDS molecules with atoms nearer than 1.5 Å from any PS chain atom were removed from
the simulation box. As each oligomer has a \( \text{SO}_4^- \) group in each terminal monomer, the number of \( \text{SO}_4^- \) groups per leaflet is 4 and 9, respectively. These systems are intended to mimic the real nanoparticle surface with surfactant as described in the Supporting Information file (see SI Section S.3). (3) In order to model the grafted copolymers present in the carboxylate-modified nanoparticles, an \( \text{H} \) atom of the outer styrene monomers is substituted by a small acrylate copolymer of variable number and monomer composition. The selected functionalities are acrylic acid (MAA), methyl methacrylate (MMA) and n-propyl methacrylate (PMA). Different copolymers have been built to change the ratio monomer surface/charge on the bilayer model, acting as “hairs” on the surfaces. For example, the system O1 is built using MAA, short monomer with negative charge, in which the ratio monomer surface/charge remains low. On the other hand, the O4 models are characterized by a high monomer surface/charge ratio. These systems are intended to mimic the real functionalized nanoparticle surface (PS-CO\(_2^-\) system, see SI Section S.3). Na\(^+\) ions were selected in accordance with the materials used in the experimental part. Although it is already known that other ions, as K\(^+\), can make a difference,\(^{26}\) it may be expected that the hydrophobic driven interaction between nanoparticle and polymer would be similar whether K\(^+\) ions were considered instead. Table 2 gives the details about the configuration of each system.

Table 2. Composition of Each Simulated System\(^d\)

| surfactant | number of PS molecules | number of SDS molecules | \( \text{SO}_4^- \) grafted oligomer composition on each PS oligomer side |
|------------|------------------------|-------------------------|---------------------------------------------------------------------|
| SDS        | 0                      | 288                     |                                                                     |
| PS-\( \text{SO}_4^-\) | 64                     | 0                       |                                                                     |
| PS-\( \text{SO}_4^-\) free | 4                     | 254                     |                                                                     |
| PS-4-SDS  | 9                      | 125                     |                                                                     |
| PS-9-SDS  | 9                      | 198                     | 3 MAA                                                              |
| PS-CO\(_2^-\) | 4                      | 248                     | 3 MAA                                                              |
| O1-4-SDS  | 9                      | 198                     | 3 MAA                                                              |
| O2-4-SDS  | 4                      | 248                     | 1 MAA, 2 MMA                                                     |
| O2-9-SDS  | 9                      | 198                     | 1 MAA, 2 MMA                                                     |
| O3-4-SDS  | 4                      | 252                     | 1 MAA, 2 MMA, 3 PMA                                              |
| O3-9-SDS  | 9                      | 207                     | 1 MAA, 2 MMA, 3 PMA                                              |
| O4-4-SDS  | 4                      | 240                     | 2 MAA, 4 MMA, 6 PMA                                             |
| O4-9-SDS  | 9                      | 180                     | 2 MAA, 4 MMA, 6 PMA                                             |

\(^{d}\) \( \text{CO}_2^- \) based monomers: acrylic acid (MAA), methyl methacrylate (MMA) and n-propyl methacrylate (PMA).

**Force Field and Simulation Protocol.** The well-established OPLS-AA and LOPLS-AA force fields have been used for all the simulations.\(^{26−28}\) In particular, improved parameters for the SDS molecules were taken from refs 26−28. The molecular dynamics simulations were performed taking into account the following common options: NPT (\( P = 1 \text{ atm} \) and \( T = 300 \text{ K} \)). V-rescale thermostat was used in the simulations,\(^{27}\) this is an extension to Berendsen coupling by adding a stochastic term that ensures a proper canonical ensemble.

Coulomb potential was evaluated using Particle Mesh Ewald (PME) with a Fourier grid spacing of 0.16. A cutoff of 1 nm was used for coulomb and van der Waals interactions.\(^{30,31}\) For each system described in the previous section, the following computational steps were applied:

1. Minimization of the whole system to relief bad contacts or forced molecular topology. The L-BFGS minimization procedure was used with a convergence criterion of maximum force below \( 10^3 \text{ kJ mol}^{-1}\text{nm}^{-1} \).
2. 1 ns molecular dynamics with position restraint on all solute atoms. The interaction energy between water molecules and solute takes around 200 ps to relax.
3. 20 ns of NPT simulation in the same conditions. The density of the bilayer model stabilized within few nanoseconds of the simulation. The surface area per SDS molecule also converged to a plateau value around the same time. The different interaction energy components stabilize within the same amount of time.
4. The final structure of the previous step is selected for further processing. Solvent molecules and counterions are deleted. Ten PEO oligomers containing 10 monomers each are randomly inserted in the empty box space above and below the slab. The resulting system is resolvated and counterions added again to neutralize the system.
5. Minimization and position restraint dynamics are performed as described in points 2 and 3 of the protocol.
6. Finally, production run is performed. Two replicas of 400 ns NPT molecular dynamics simulation for each system are performed in the conditions above-described.

### RESULTS AND DISCUSSION

**Electrophoretic Mobility and Dynamic Light Scattering.** A full characterization of the PEO sample and the optical probes used in this work has been performed. The specific details can be found in the SI. If an interaction exists between the PEO molecules and the probe particles, the surface net charge of the later should change depending on the degree of particle coverage and on the polymer nature. Additionally, the experiments should be performed at suitable concentrations of both tracer particles and polymer. This means that the polymer concentration should be low enough for the nature of the particle surface not to be screened by the polymer. For this reason, we have performed measurements at a given particle concentration (\( c_p = 0.1\% \text{ w/v} \)) and variable polymer concentration in the dilute regime (\( c < \approx 0.5 \text{ mg mL}^{-1} \)). The results obtained for \( \mu_e \) in both PEO/PS-\( \text{SO}_4^- \) (100 nm) and PEO/PS-CO\(_2^-\) (150 nm) systems in the whole PEO concentration range explored are shown in Figure 1. It is observed that in the case of PS-CO\(_2^-\) nanoparticles a strong decrease of \( \mu_e \) toward the corresponding value obtained for the

![Figure 1](https://doi.org/10.1021/acs.langmuir.0c02715)

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bare PS-SO$_4^-$ particles is observed as the PEO concentration decreases, which reflects the lack of interaction between the PEO macromolecules and the sulfate functionalized particles (Figure 1A). In this case the PEO chains screen the probe particles surface charge for polymer concentrations higher than 0.1 mg mL$^{-1}$, for the selected particle concentration of 0.1% (w/w). Below this threshold an abrupt change of $\mu_s$ value takes place, and reaches the measured value of the bare PS-SO$_4^-$ for PEO concentrations well below 0.01 mg mL$^{-1}$. On the contrary, in the case of PS-CO$_2^-$ the values of $\mu_s$ remains around the corresponding value of PEO in the entire polymer concentration range explored, a result that clearly indicates that the polymer macromolecules are firmly anchored to the particle surface (Figure 1B).

The value of $\mu_s$ obtained for PEO/PS-CO$_2^-$ systems, even at very low concentration of PEO ($c \sim 3.0 \times 10^{-3}$ g mL$^{-1}$), is in agreement with those reported in covalently PEGylated nanoparticles of different nature.$^{32-34}$ It should be recalled here that given the $\mu_s$ and $t_e$ values of the bare nanoparticles, the charge surface density is almost the same for both PS-CO$_2^-$ and PS-SO$_4^-$ systems. Also, the hydrodynamic size of both particles is not very different, so in the absence of interactions between PEO chains and particles, the critical concentration to cancel the screening effect of the polymer over the surface charge of the particles should be also similar.

This critical concentration should depend in principle on the total surface of the particles, $S_p$, and then on their size, $r_p$, and concentration, $c_p$, but also on the size of polymeric chains, given by $r_g$. On one hand, we may assume that the necessary number of molecules per volume unit to shield the surface is given by $N_m = c_p N_p/M_w$. On the other hand, the total surface per volume unit can be obtained by $S_T = N_p S_p$ being $N_p$ the number of particles per volume unit $N_p = 3c_p/4\pi r_p^3$ and $S_p$ the surface of a particle $S_p = 4\pi r_p^2$. The ratio between $S_T$ and $N_m$ around the critical concentration should be of the order of $r_g^2$. At a given particle fractional volume in the solution, $c_p/\rho_p$ the critical concentration, $c_{sw}$ scales as $M_w/\rho_p r_g^2$. This calculation, considering the experimental conditions used here ($c_p = 0.001$ mg mL$^{-1}$) and the particle and PEO hydrodynamic and molecular properties gives rise to a value of $c_{sw} = 2.5 \times 10^{-3}$ mg mL$^{-1}$ for PEO300 which is satisfactorily close to that obtained from electrophoretic mobility experiments, as it can be observed in Figure 2.

It should be noted that decreasing the particle concentration to $c_p = 0.0001$ mg mL$^{-1}$ leads to a value of $c_{sw} = 2.4 \times 10^{-4}$ mg mL$^{-1}$ for PEO, a fact also proved experimentally in Figure 2. Additional experiments have been performed by using PS-SO$_4^-$ particles ($c_p = 0.001$ mg mL$^{-1}$) with a hydrodynamic radius of $r_g = 35$ nm (see SI archive). The proposed scaling above gives rise in this case to a value of $c_{sw} = 8.3 \times 10^{-5}$ mg mL$^{-1}$, which is also close to the experimental results shown in Figure 2. These results have a crucial practical importance, as to determine the possibility of interaction between a particular particle/polymer pair from electrophoretic mobility experiments, the specific polymer concentration to avoid macro-molecular shielding onto particle surface should be carefully chosen, depending mainly on particle size and concentration.

PEO is a flexible linear polymer, and if the macromolecules are physically bound to the particle surface, they can dramatically influence the Brownian motion of the PS-CO$_2^-$ particles by introducing additional frictional drag and thus reducing particle diffusivity. Then we have further explored the hydrodynamic properties of the systems in the dilute concentration region, in order to get an additional probe about the polymer/particle interaction. In Figure 3, we can observe the autocorrelation function obtained from DLS experiments in particle-polymer systems for a concentration of PEO of $c = 2 \times 10^{-3}$ mg mL$^{-1}$.

It can be clearly observed that the autocorrelation function obtained for the PEO/PS-SO$_4^-$ system is virtually the same as that observed for the bare PS-SO$_4^-$ probe particles (inset in Figure 3). This result is expected if no interaction exists between PEO and PS-SO$_4^-$ particles, assuming that the viscosity of the solution is not greatly affected by such a low concentration of PEO300. On the contrary, the autocorrelation function of the PEO3/PS-CO$_2^-$ system clearly shifts toward higher lag times, a result that indicates a measurable decrease of the diffusion coefficient of the probe particles in identical conditions. The evaluation of the autocorrelation function by means of the cumulant analysis gives a value for the diffusion...
coefficient $D = 0.150 \mu m^2/s^{-1}$ and an effective hydrodynamic radius $r_{\text{eff}} = 163.0$ nm for the PS-CO$_3^-$ systems. This result is consistent with the presence of a bound PEO layer on the probe surface with a thickness of around 15 nm. It is worth to note that this increase is one-half the hydrodynamic size of PEO chains (see Table 1 and SIE).

**Computer Simulations.** Two descriptors are used along this work to characterize the interaction between the bilayer model and the PEO polymer solution. The first one is the so-called “Parking Area” (PA), which represents the average surface area per charge present on that surface:

$$PA = \frac{\text{SASA}_{\text{bilayer}}}{\text{number of negative charge on the surface}}$$

This descriptor can be stated as a measure of the charge density on the surface. The solvent accessible surface area (SASA) is used in this work to estimate the bilayer and polymer surface areas. The second one is the intermolecular contact area (IA) between the bilayer model and the polymer. This value is calculated as the inaccessible area to solvent owing to the contact between nanoparticle and PEO surfaces. The following equation can be used to calculate the interaction area based on Solvent Accessible Surface Area (SASA) estimations:

$$IA = \frac{\text{SASA}_{\text{bilayer}} + \text{SASA}_{\text{PEO}} - \text{SASA}_{\text{bilayer+PEO}}}{2}$$

SASA$_{\text{bilayer}}$, SASA$_{\text{PEO}}$, and SASA$_{\text{bilayer+PEO}}$ are the SASAs calculated for the one leaflet of the bilayer model, the PEO oligomers and the bilayer+PEO system, respectively.

SASA values are needed to calculate both the PA and IA. In this work, SASA is calculated using the method described by Eisenhaber et al., taking into account the approximate water radius (0.14 nm) for the solvent probe.

A schematic representation of the IA calculation based on SASA values is shown in Figure 4. Each system is solvated with TIP4P water molecules excluding the hydrocarbon region inside the slab. Counterions are added accordingly to yield neutral systems. For each frame, the SASA is calculated on the slab alone (Figure 4A), on all the PEO oligomers (Figure 4B), and finally on the adsorbed complex and the unadsorbed PEO molecules (Figure 4C). Time evolution of SASA$_{\text{bilayer}}$, SASA$_{\text{PEO}}$, and SASA$_{\text{bilayer+PEO}}$ for PS-SDS-free nanoparticle is illustrated as an example in Figure 5.

Initially, the NP slab and the PEO oligomers are spatially separated so that the SASA$_{\text{bilayer+PEO}}$ is approximately the sum of SASA$_{\text{bilayer}}$ and SASA$_{\text{PEO}}$. As the system evolves, the SASA$_{\text{bilayer+PEO}}$ decreases due to the adsorption of PEO molecules on the NP surface. Keep in mind that, this slab corresponds to SO$_4^-$ capped PEO oligomers as a representation of the PS-SO$_4^-$ nanoparticle surface. Furthermore, this SASA value can be considered as a measurement of the contact between PEO chains and the nanoparticle. Thus, the separated species show a stable value along the simulation whereas polymer–nanoparticle interactions take around 100 ns to reach a plateau value, after that this value keeps stable. Similar observations were obtained with the other replicas and/or systems considered in this study (not shown).

Two pure bilayer are first simulated, one containing only SDS molecules (SDS) and one composed by PS-SO$_4^-$ oligomers (PS-SDS free). The simulation of SDS is due to the fact that it is the surfactant used in the synthesis of polymer nanoparticle (see SI S3). The SDS slab presents a PA of 0.57 ± 0.02 nm$^2$/charge group, slightly larger than the value reported for the estimated area per SDS molecule at adsorption saturation (0.52 nm$^2$). Furthermore, the average IA corresponding to the last 100 ns of the PEO-included MD simulation for this system gives a value near 0 (0.2 ± 0.3 nm$^2$), that is, there is no interaction between the polymer and the SDS slab. Likely, this is due to the high order observed on the bilayer surface, in which the SO$_4^-$ groups are homogeneously distributed on the surface (low PA value) screening the hydrophobic interactions between SDS and PEO chains.

On the other hand, the PS-SDS free model gives a value of PA around 1.87 ± 0.02 nm$^2$/charge group, pointing to a decrease of the charge density on the surface. The atomistic simulation of the interaction between PS-SDS free and the PEO oligomer chains yields an IA of 47 ± 1 nm$^2$. This value can be compared with the calculated SASA for the 10 PEO oligomers (84 ± 4 nm$^2$). The IA value is more than half the value of the total accessible surface of the PEO molecules, being indicative of a strong interaction between the two compounds. This interaction can be visualized in Figure 7A, where most of the PEO chains are in close contact with the hydrophobic areas of the bilayer model. Hence, PEO chains are able to enter through the charged slab to reach the hydrophobic backbone of the PS chains. In principle, this is in contrast to the lack of interaction between the PS-SO$_4^-$ and the PEO polymer observed in the experimental section.

As a consequence of the emulsion polymerization process used to synthesize the PS nanoparticles, SDS molecules can
remain trapped on the nanoparticle surface with the sulfate moieties exposed to the hydrophilic phase (see SI Section S.3). Therefore, we have simulated the nonfunctionalized PS-\(\text{SO}_4^−\) systems as slabs containing SDS molecules and PS oligomers. The SDS:PS oligomers ratio considered in the model bilayer systems can be estimated in the following way: On one hand, the nanoparticle surface is around \(1.25 \times 10^5 \text{ nm}^2\) given the nanoparticle sphere diameter of 200 nm. Taking into account the estimated area per SDS molecule at adsorption saturation (0.52 nm\(^2\)), we obtain around \(2.4 \times 10^5\) SDS molecules on the nanoparticle surface. On the other hand, given the density of polystyrene (\(\rho = 1.05 \text{ g cm}^{-3}\)) the nanoparticle volume (\(V \approx 4 \times 10^6 \text{ nm}^3\)), and the PS molecular weight (\(M_w \approx 300 \text{ kg mol}^{-1}\)) the number of PS molecules can be calculated with the following formula:

\[
N_m = \frac{(V \rho) \cdot 10^{-21}}{\left(\frac{M_w}{N_A}\right)}
\]  

where \(N_A\) is the Avogadro’s number and \(N_m\) is the number of PS molecules in the nanoparticle. The numerator accounts for the nanoparticle mass whereas the denominator accounts for the PS molecule weight, both expressed in grams. This results around 8000 PS molecules on each nanoparticle, giving a proportion of 30 SDS molecules per PS chain. As shown in Table 2, we have built two sets of systems with a ratio of around 30, close to the above estimation, and 10, approximately. The close packing of SDS surfactant molecules forms a bilayer in which the PS oligomers are embedded with approximately. The close packing of SDS surfactant molecules around 30, close to the above estimation, and 10, a proportion comparable with the real nanoparticle ratio area \((0.2 \pm 0.3 \text{ nm}^2)\), that is, there is no interaction between the polymer and the NP model.

The SDS:PS ratio is around 30 on each bilayer face, which is a proportion comparable with the real nanoparticle ratio area taking into account the nanoparticle surface (\(1.25 \times 10^5 \text{ nm}^2\)), the number of PS chains per nanoparticle (\(\approx 10^4\)) and the estimated area per SDS molecule at adsorption saturation (0.52 nm\(^2\)). The PS-CO\(_2^−\) functionalized latex nanoparticles, several combinations of grafted oligomer compositions and SDS:PS ratios were taken into account (Table 2). The grafted oligomers were inserted in a SDS so that the hydrophilic groups interact with the water phase (Figure 7C). The acrylic acid groups form a kind of multianionic “hairs” spread over the nanoparticle surface. It is expected that the number of charges increases respect to the nonfunctionalized nanoparticle due to the contribution of each charged monomer. However, at the same time, the accessible surface increases too due to the exposition of the copolymer chains to the hydrophilic phase. To take into account this, we have built four different functionalized models (O1–O4). The O1 and O2 models contain charged MAA and MMA monomers. These systems have a low ratio surface area/charge. In these systems, the interaction with the PEO polymer is very similar to the interaction already discussed for the PS-\(\text{SO}_4^−\) system.

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Regarding the PS-CO\(_2^−\) functionalized latex nanoparticles, several combinations of grafted oligomer compositions and SDS:PS ratios were taken into account (Table 2). The grafted oligomers were inserted in a SDS so that the hydrophilic groups interact with the water phase (Figure 7C). The acrylic acid groups form a kind of multianionic “hairs” spread over the nanoparticle surface. It is expected that the number of charges increases respect to the nonfunctionalized nanoparticle due to the contribution of each charged monomer. However, at the same time, the accessible surface increases too due to the exposition of the copolymer chains to the hydrophilic phase. To take into account this, we have built four different functionalized models (O1–O4). The O1 and O2 models contain charged MAA and MMA monomers. These systems have a low ratio surface area/charge. In these systems, the interaction with the PEO polymer is very similar to the interaction already discussed for the PS-\(\text{SO}_4^−\) system.

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presents more hydrophobic surface contributed by the uncharged carboxyl monomers ready to interact with the polymer.

Figure 7C shows the final snapshot of this simulation depicting the specific interaction between the grafted copolymer chains and the PEO oligomers. Our calculations suggest that the higher the number of charged acrylic acid monomers that are included in the grafted copolymer composition, the lower the PA and consequently the lower the interaction with the polymer. This can be illustrated by the O1–4-SDS system composed by four PS oligomers each grafted with three charged MAA monomers on both slab sides and inserted into the SDS bilayer. In this case the PA is 0.60 ± 0.01 nm²/charge group and the resulting IA is negligible (0.2 ± 0.3 nm², see Table 3). It can also be observed that the larger number of charged acrylic acid monomers in the copolymer chains, the larger the fraction of PS oligomers in the slab composition, the lower the PA and consequently the lower the interaction with the polymer. More importantly, the atomistic simulation models developed in the present research allowed a clear interpretation of our experimental observations in terms of interactions between polymeric chains and nanoparticles. The results obtained point to the importance of computer simulations in determining the type of interactions that can take place between polymeric systems and particles. Thus, the combination of both the design of the nanoparticle together with the computer simulations may help in the selection of suitable nanoparticles for microrheological measurements. A couple of suggestions can be made regarding nanoparticle design, including the use of different types of materials (metallic, ceramic, polymeric, and hybrid nanoparticles), and different approaches for surface functionalization, as grafting with short copolymer chains and/or incorporating monomers with charged groups to dismiss the interactions between polymeric chains and nanoparticle surface.

### CONCLUSIONS

Using light scattering, we measure the electrophoretic mobility and diffusion coefficient of carboxylate-modified and sulfate latex particles in PEO solutions. The results show a bound PEO layer on the carboxylate-modified polystyrene particles, as the surface net charge vanishes even at very low PEO concentration. In addition, this layer causes a slower diffusion than that corresponding to the bare particles. We show that the diffusion is the result of a significantly increased effective particle size $2\eta_{PEO} = 30$ nm for the PEO sample studied. This bound layer is not present in sulfate latex particles, which closely follow the Einstein-Stokes law for diffusion. The interaction between the carboxylate-modified surface and the PEO macromolecules has been confirmed by means of atomistic computer simulations. The grafted acrylate copolymer with a high surface/charge ratio confer more hydrophobic surface ready to interact with the polymer. The simulations suggest that the interaction is modulated by the nature of the acrylic acid monomer and the length of the grafted copolymer. More importantly, the atomistic simulation models developed in the present research allowed a clear interpretation of our experimental observations in terms of interactions between polymeric chains and nanoparticles. The results obtained point to the importance of computer simulations in determining the type of interactions that can take place between polymeric systems and particles. Thus, the combination of both the design of the nanoparticle together with the computer simulations may help in the selection of suitable nanoparticles for microrheological measurements. A couple of suggestions can be made regarding nanoparticle design, including the use of different types of materials (metallic, ceramic, polymeric, and hybrid nanoparticles), and different approaches for surface functionalization, as grafting with short copolymer chains and/or incorporating monomers with charged groups to dismiss the interactions between polymeric chains and nanoparticle surface.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.0c02715.

Experimental details, polymer, and nanoparticles characterization (molecular weight, hydrodynamic size and electrophoretic mobility), and details about the construction of nanoparticle surface for simulations (PDF)

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#### Table 3. Parking Area and Interaction Area for Each System Described in Table 2

| System       | Parking Area (Å²) | Interaction Area (nm²) |
|--------------|-------------------|------------------------|
| Surfactant   |                   |                        |
| SDS          | 57 ± 2            | 0.2 ± 0.3              |
| PS-SO₄⁻      |                   |                        |
| PS-SDS free  | 187 ± 2           | 47 ± 1                 |
| PS-4-SDS     | 61 ± 1            | 0.2 ± 0.3              |
| PS-9-SDS     | 80 ± 1            | 7 ± 2                  |
| PS-CO₂⁻      |                   |                        |
| O1–4-SDS     | 60 ± 1            | 0.2 ± 0.3              |
| O1–9-SDS     | 66 ± 1            | 5 ± 2                  |
| O2–4-SDS     | 68 ± 1            | 5 ± 1                  |
| O2–9-SDS     | 81 ± 1            | 6 ± 3                  |
| O3–4-SDS     | 75 ± 1            | 11 ± 4                 |
| O3–9-SDS     | 95 ± 2            | 19 ± 2                 |
| O4–4-SDS     | 93 ± 1            | 36 ± 2                 |
| O4–9-SDS     | 129 ± 2           | 41 ± 3                 |
Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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