

Improving Tracer Particle Surface Properties for Wind Tunnel Research

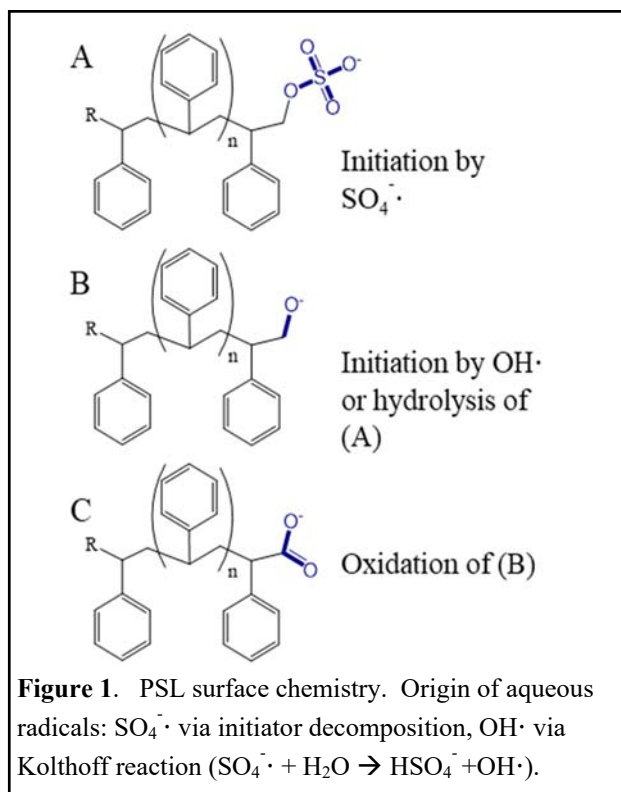
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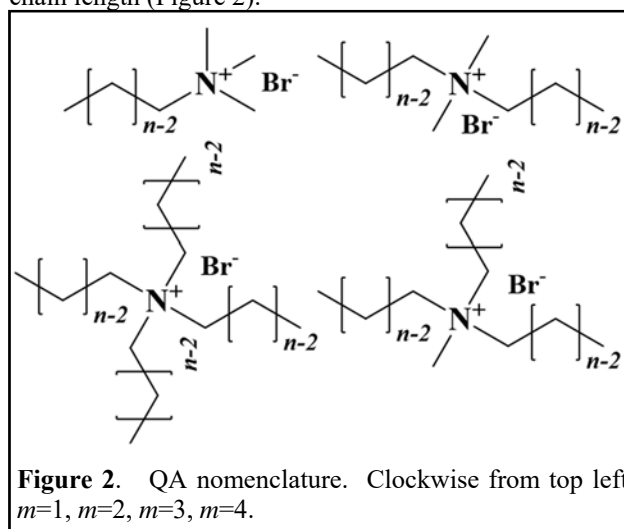
Introduction

The surface properties of micron size polystyrene latex microspheres (PSLs) modified with quaternary alkylammonium (QA) surfactants were investigated, with a focus on the relationship between surface chemistry and adhesion. These investigations were motivated by the need to develop non-fouling tracer particles for wind tunnel studies. The goals were to relate the work of adhesion between particles and substrates to the type and amount of QA modifier in order to optimize the performance of PSL tracers.

Surfactant-free emulsion polymerization (SFEP) can produce PSLs for wind tunnel tracers. Covalently-bound charged groups (derived from the initiator) stabilize PSL surfaces in water. This work used PSLs with anionic surface groups (Figure 1). Previous studies indicated that surface-bound charged groups on PSLs have a significant impact on their interfacial energy^[1]. Modifying charged surface groups therefore offers a method to modulate PSL interfacial properties. In this work, PSLs and films were modified by adsorption of QA surfactants.



Polystyrene (PS) thin films were sulfonated and used as model substrates of PS surfaces bearing anionic groups. QA adsorption to PSL surfaces is driven by either electrostatic association between negatively charged PSL surface groups and positively charged ammonium head groups, or by hydrophobic interactions between hydrocarbon alkyls in QAs and the PSL surface^[2]. Both the number of alkyl chains per QA, m , and the carbon atoms per chain, n , were varied to isolate effects due to chain number and chain length (Figure 2).



Experimental

A series of PSLs, 0.5-1 μm in diameter, were prepared by SFEP at 70°C using potassium persulfate (KPS) as an initiator^[3]. Final particle size and surface charge density were varied between batches by adding different amounts of KPS, magnesium sulfate, sodium hydroxide, and sodium bicarbonate at the beginning of the reaction. Latexes were cleaned by serum replacement using deionized water, followed by 10⁻⁴ M hydrochloric acid (HCl), and followed by more deionized water. Serum replacement continued until the filtrate conductivity was <1 $\mu\text{S}/\text{cm}$. QA modification was achieved by dissolving a measured amount of QA in a latex and stirring for 24 hr. Excess QA was removed by three cycles of centrifuging and resuspending the particles in deionized water.

PS films were produced by spin-coating polystyrene onto silicon wafers from toluene. The films were sulfonated by immersion in 96% sulfuric acid for up to ten

minutes, then rinsed with deionized water and dried. QAs with $n=6-18$ and $m=1-4$ were used as received. QA solutions for film functionalization were prepared at concentrations between 0.5 and 80% of their critical micelle concentration (CMC). Sulfonated PS films were immersed in QA solutions for up to 24 hours and then rinsed in deionized water to remove any weakly-adsorbed QAs before drying.

Water contact angle (θ , Model 100-00 Goniometer, Ramé Hart) and ellipsometry measurements (VASE, J.A.Woollam Co.) were collected on pristine, sulfonated and QA-modified films. Ellipsometry results showed no significant changes to film thickness after sulfonation.

PSLs in dilute suspensions of deionized water were characterized by light scattering with a Zetasizer Nano (Malvern Instruments) to determine particle size and electrophoretic mobility (μ_e). Conductometric titrations were carried out to characterize PSL surface groups. Nitrogen gas was bubbled through PSL suspensions before and during titration to exclude CO_2 . Titrants were added to the sample through glass capillaries. Typically, two cycles of forward (NaOH) and backward (HCl) titrations were carried out on each sample.

Results and Discussion

Spin-coated PS films were between 50 and 60 nm thick. Differences in film thickness before and after sulfonation and QA modification were within instrument error. Water contact angles on all pristine films (θ_0) were $\sim 90^\circ$, as expected. Contact angles after sulfonation (θ_s) were between 55 and 60°, indicating that sulfonation increased the hydrophilic character of the surface. $\Delta\theta_{0s}$ ($\Delta\theta_{0s} = \theta_0 - \theta_s$) was independent of acid exposure time, suggesting the maximum surface concentration of acid groups was reached in less than one minute. Reusing the same acid bath eventually led to a decreased $\Delta\theta_{0s}$. We found that a 50 ml bath should be reused no more than 10 times for consistent $\Delta\theta_{0s}$ values. θ values after functionalization (θ_f) were intermediate to the pristine and sulfonated values. Thus, QA functionalization increased the hydrophobic nature of the sulfonated surface, but not to the extent of pristine PS. $\Delta\theta_{fs}$ ($\Delta\theta_{fs} = \theta_f - \theta_s$)

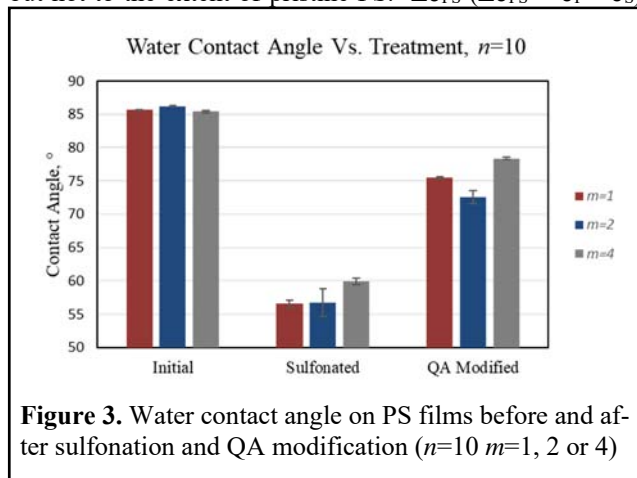


Figure 3. Water contact angle on PS films before and after sulfonation and QA modification ($n=10$ $m=1, 2$ or 4)

values were typically between 15 and 22° (Figure 3). Detailed correlations regarding the relationship between QA structure and surface properties of modified films are not yet available.

Most batches of PSLs were monodisperse with average particle diameters between 0.5 and 1 μm . Some latexes synthesized using high initiator concentrations and in the presence of NaOH were polydisperse or bimodal. For the monodisperse latexes, electrophoretic mobilities were between -2 and -6 $\mu\text{Scm/Vs}$. Differences in μ_e between latexes of similar size were attributed to variations in the number and type of surface-bound charged groups.

Conductometric titration data were analyzed using the method of Labib & Roberts^[4]. Titrations indicated the presence of both strong and weak acids on PSL surfaces, with a total area density on the order of 0.1 to 1 acid group per nm^2 . The fraction of total titratable groups that were strong acid groups varied between batches from ~ 0 to >0.8 . Figure 4 shows a single forwards-backwards titration curve. Repeated forwards-backwards titrations on the same sample typically exhibited good reproducibility.

These results indicate that we have successfully created a 'library' of PSLs with comparable sizes but variations in the total concentration of charged surface groups and the ratio of strong (sulfate) to weak (carboxyl) charged groups.

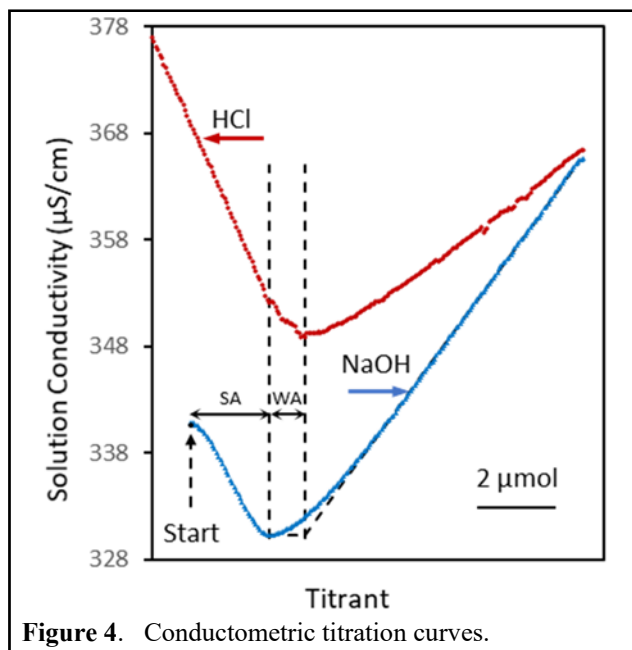


Figure 4. Conductometric titration curves.

Future Work

Future studies with thin films will investigate how surface acid concentration and QA structure affect QA loading and film interfacial properties. Wafers with PS films will be dipped into acid at a constant rate to create gradients in the concentration of surface acids. Gradient films will be equilibrated in dilute QA solutions ($[\text{QA}] \ll \text{CMC}$) and rinsed to remove weakly adsorbed QAs. The concentration of sulfur (from sulfonate groups) and nitrogen (from QAs)

will be measured along the gradient using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The relative number of sulfonate and QA species will clarify the stoichiometry of QA/sulfonate association and limiting behavior at different acid group concentrations. The surface area per adsorbed QA will be calculated to comprehend the conformation of the alkyl tail(s) at different loading (Figure 5).

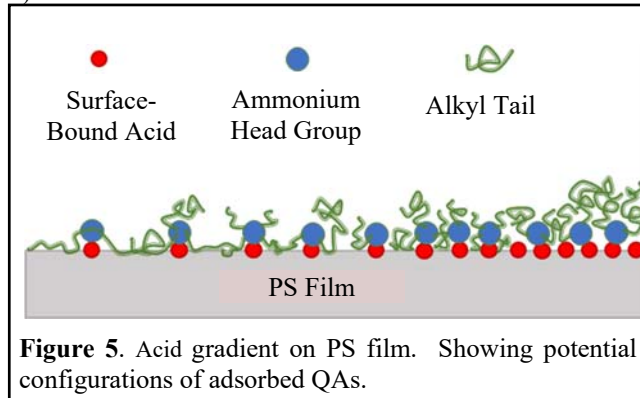


Figure 5. Acid gradient on PS film. Showing potential configurations of adsorbed QAs.

The PSL library produced from this work provides a variety of PSL surface chemistries that enable further investigations into the relative impacts of initial surface chemistry and QA modifications on the final properties of modified PSLs. These PSLs will be used to optimize the modification process and modified PSLs will be tested to characterize their interfacial properties and adhesion to surfaces.

To create stable substrates for contact angle measurements, dry PSL powders will be compressed into a pellet using a hydraulic press. Contact angle measurements will be used to relate PSL modification with changes in PSL hydrophilicity^[1]. Finally, we will directly measure the work of adhesion of PSLs on substrates using atomic force microscope (AFM) measurements. We developed a custom method for making AFM colloidal probes using PSLs for this purpose; it will be the subject of a later publication.

QA adsorption isotherms will be collected by equilibrating known amounts of PSL in QA solutions. After removing PSLs by centrifugation, equilibrium concentration of QA in the surfactant will be determined from surface tension measurements, and the surface loading of QA on the PSLs determined from a mass balance. Measurements of PSL μ_c in QA solutions will be used to determine the effect of QA adsorption on particle charge and stability. Previous investigations reported different trends in the shape of μ_c vs. [QA] curves based on the structure of the QA used^[2,5]. We will independently vary the n and m values of QAs to further clarify the relationship between adsorption, charge and structure.

Conclusions

We synthesized and characterized a library of PSLs with various concentrations of surface-bound acid groups. We also produced PS films bearing sulfonate groups and demonstrated adsorption of QA molecules to

those surfaces. Adsorbed QAs are stable in water and increase the hydrophobic character of sulfonated films. For the next stage of this research, we propose using sulfonate gradients on PS films to identify trends and limiting behavior for QA adsorption. We identify methods to monitor QA/PSL association during PSL modification and describe techniques to characterize the interfacial properties of modified PSLs.

References

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