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Poly(acrylic acid)–Poly(ethylene oxide) Comb Polymer Effects on BaTiO₃ Nanoparticle Suspension Stability

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We have studied the effects of poly(acrylic acid)–poly(ethylene oxide) (PAA–PEO) comb polymers on the stability of aqueous BaTiO₃ nanoparticle suspensions over a wide pH range in the presence and absence of mono- and divalent salt species. The comb polymer architecture consists of charge-neutral PEO teeth attached at random intervals along an ionizable PAA backbone. Potentiometric titrations, light scattering, and turbidity measurements were conducted on pure PAA and PAA–PEO solutions to assess their degree of ionization, radius of hydration, and stability. Adsorption isotherm and rheological measurements were conducted on BaTiO₃ nanoparticle suspensions to determine the effectiveness of both PAA and PAA–PEO dispersants. Our observations indicate that the presence of PEO teeth effectively shield the underlying PAA backbone from ion interactions, e.g., counterion-screening or ion-bridging effects, thereby allowing PAA–PEO dispersants to impart stability to BaTiO₃ nanoparticle suspensions over a wide range of pH, ionic strength, and ion valency conditions where pure PAA fails.

I.   Introduction

POLYELECTROLYTE species, such as poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA), are widely used dispersants that impart electrosteric stabilization to colloidal suspensions.[1,2] These species contain ionizable carboxylic acid (COOH) groups (one per monomer unit) along their backbone. Such groups dissociate to form negatively charged carboxylate groups (COO⁻) with increasing pH ($pK_a \sim$ 4.5–5). The degree of ionization strongly affects their hydrodynamic radius, R_H, in solution, as well as their thickness, ($\delta \sim R_H$) when adsorbed on colloid surfaces. Both the degree of ionization and adlayer thickness influence the ability of polyelectrolyte species to stabilize colloidal suspensions.[3]

Recently, significant attention has been directed toward understanding how polyelectrolyte species interact with oppositely charged ions (counterions) in solution as well as what role this may play in governing their phase behavior, assembly, and structure.[4–11] Ion interactions can induce changes in adlayer thickness[6–9] or promote polymer association through ion bridging.[4,10,11] These effects, which intensify as the counterion concentration and valency increase, may induce dramatic changes in system stability.

During colloidal processing, the concentration of ions in solution may rise due to several contributions. First, salt species may be intentionally added to regulate colloidal forces.[12] For example, Li and Jean[5] recently demonstrated that the stability of aqueous barium titanate suspensions dispersed by PAA was dramatically reduced upon the addition of Ba²⁺ ions in solution. Second, ion dissolution or leaching from the ceramic particle surfaces may occur. In the case of BaTiO₃, Ba²⁺ ion dissolution increases with decreasing pH leading to a significant buildup of such species in solution. Such phenomena limit the pH range over which aqueous BaTiO₃ suspensions may be processed to neutral pH values or higher.[5] The extent of dissolution of a given particle in suspension is strongly influenced by its radius, a,[13] and volume fraction, ϕ.[14] Thus, a rapid buildup of ions may occur when processing concentrated nanoparticle suspensions. To overcome these challenges, there is a need to develop new dispersants for ceramic processing, such as those based on a comb polymer architecture.[15,16]

Here, we investigate the influence of comb polymers, comprised of a PAA backbone and charge-neutral poly(ethylene oxide) (PEO) teeth, on the stability of barium titanate (BaTiO₃) suspensions over a wide range of pH and ionic strength conditions. As a benchmark, we compare our observations to those obtained for BaTiO₃ suspensions stabilized by pure PAA. Our observations reveal two important differences between pure PAA and PAA–PEO comb polymers. First, the presence of PEO teeth attached at random intervals along the PAA backbone prevents large conformational changes in solution or on colloidal surfaces in response to varying pH or ionic strength. Second, PEO teeth protect the underlying PAA backbone from ion interactions that promote aggregation of pure PAA species in solution or PAA-coated BaTiO₃ nanoparticles in suspension. As a result, PAA–PEO comb polymers impart stability to colloidal suspensions over a wide range of pH and ionic strength conditions where pure PAA dispersants fail.

II.   Experimental Procedure

(1)   Materials System

BaTiO₃ nanoparticles (BT-16 K-Plus, Cabot Co., Boyertown, PA) served as the ceramic powder in this study. These species had a mean radius, a, of 30 nm, a specific surface area of 16.4 m²/g, and a density of 5.88 g/cm³, as determined by scanning electron microscopy (SEM), nitrogen gas adsorption isotherm, and helium pycnometry, respectively. An anionic polyelectrolyte, PAA (Polyscience, Inc., Warrington, PA) with an average molecular weight of 5000, and a comb polymer (PAA–PEO) (W. R. Grace & Co.—Connecticut, Cambridge, MA) consisting of an anionic PAA backbone (5000 MW) and charge-neutral PEO teeth (2000 MW) served as dispersants in this study (see Fig. 1). The weight- and number-average molecular weights for the PAA–PEO comb polymer was determined to be 25 800 and 8380 using gel permeation chromatography (GPC). Note, a PEO standard (American Polymer Standards Corp., Mentor, OH) was used for GPC analysis, and the solvent was an aqueous, potassium nitrate solution (0.01M). PAA and PAA–PEO have an average of 71 and 57 ionizable carboxylic

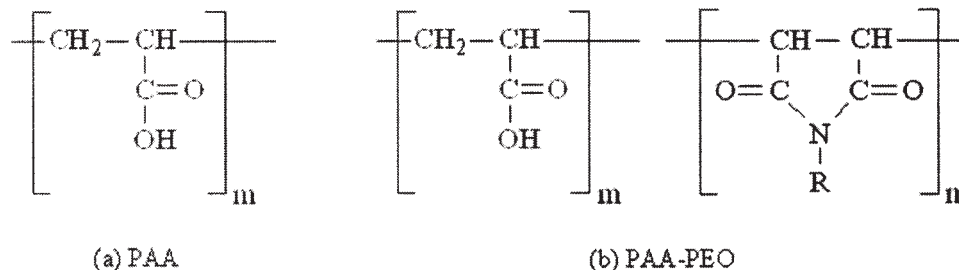**Fig. 1.** Chemical structure of (a) PAA and (b) PAA–PEO. (Note: $R = (CH_2CH_2O)_x–CH_3$, PEO.)

acid functional groups per molecule, respectively, as determined by potentiometric titration.

(2) Solution Characterization

Dilute polymer solutions were prepared by adding an appropriate amount of either PAA or PAA–PEO to deionized water to achieve a concentration, c, of 5 mg of polymer/(mL of solution). Note, this value was about an order of magnitude below the dilute-to-semidilute transition, which occurs at 47 and 53 mg of polymer/(mL of solution) for PAA and PAA–PEO, respectively, at pH 9. Stock solutions of $2M$ KCl or $0.5M$ $BaCl_2$ were prepared by dissolving either KCl (Fisher Chemicals, Fair Lawn, NJ) or $BaCl_2 \cdot 2H_2O$ salt (Fisher) in deionized water. These stock solutions were used to vary the respective monovalent or divalent salt concentration in the polymer solutions. The pH was adjusted using either a $0.1M$ HNO_3 or $0.1M$ NH_4OH solution. The polymer solutions were magnetically stirred for 0.5 h to allow for equilibration.

Potentiometric titrations were conducted on dilute PAA and PAA–PEO solutions (initial pH 3.5) to measure the pH as a function of titrant addition. The titrant species was a $2.5M$ NaOH solution, which was dosed into a continuously stirred sample in regular aliquots using an autotitrator (Microlab®500, Hamilton Co., Reno, NV). The pH response was measured using a standard silver–silver chloride electrode. Data analysis was conducted, as outlined by Arnold and Overbeek[17] and by Hunter,[18] to determine the dissociation behavior of carboxylic acid groups as a function of pH.

Dynamic light scattering measurements (Zetasizer 3000HS, Malvern Instruments, Ltd., Worcestershire, United Kingdom) were conducted on PAA and PAA–PEO solutions (pH 9) of varying salt concentration to determine their R_H as a function of counterion concentration. To ensure that the solutions were free from particulate contaminants, they were passed through a 200-nm filter into dust-free cuvettes and capped. Refractive indices, n, of 1.53 and 1.47 were used in the scattering experiments for PAA and PAA–PEO, respectively. Data analysis was conducted using the CONTIN algorithm by Provencher,[19] which provided a reasonable fit (i.e., less than 1% error).

The turbidity of PAA and PAA–PEO solutions of varying pH and salt concentration was determined by measuring the intensity of transmitted light ($\lambda = 560$ nm) through samples contained in glass cells. Dilute PAA and PAA–PEO solutions (pH 3 and 9) of varying salt concentration were prepared as described above. The raw data were normalized by the maximum and minimum transmitted intensity to determine the percent transmittance.

The concentration of free Ba^{2+} ions in PAA and PAA–PEO solutions (pH 9) of varying $BaCl_2$ salt concentration was measured using an ion-selective electrode (detectION™ electrode, Nico Scientific, Inc., Huntingdon Valley, PA). Counterion species that are bound, i.e., complexed with charged COO^- groups along the polyelectrolyte backbone, do not contribute to the solution concentration measured by this technique. The concentration of bound counterions was calculated by taking the difference between the total Ba^{2+} addition and the measured, free Ba^{2+} concentration based on a standard calibration curve.

(3) Suspension Characterization

$BaTiO_3$ nanoparticle suspensions of varying volume fraction solids, ϕ, were prepared by dispersing an appropriate amount of the ceramic powder in an aqueous dispersant solution. The solution was premixed by adding the desired dispersant amount to deionized water, followed by magnetic stirring for 0.5 h. On adding $BaTiO_3$ powder, the suspension was ultrasonicated (F550 Sonic Dismembrator, Fisher Scientific, Pardubice, Czech Republic) for 5 min using a 1-s on/off pulse sequence. The suspension pH was adjusted using $0.1M$ HNO_3 and $0.1M$ NH_4OH solutions. KCl and $BaCl_2$ stock solutions, described above, served as a source for monovalent and divalent salt additions, respectively. All suspensions were magnetically stirred for a 24-h equilibration time.

Adsorption isotherm measurements were conducted using a total organic carbon (TOC) analyzer (Phoenix 8000, Tekmar-Dohrmann), which provided a quantitative measure of the nonadsorbed fraction of either PAA or PAA–PEO in solution. In this experiment, $BaTiO_3$ suspensions ($\phi = 0.10$, pH 9) were prepared with varying dispersant concentration, mixed for a 24-h equilibration time, and then centrifuged at 2000 rpm for 10 min to separate the solids and supernatant. The supernatant was immediately decanted and diluted with deionized water for the TOC measurement. Several aliquots were taken from each sample and measured, and an average value was reported on the basis of standard calibration curves (correlation coefficient, R, was 0.998) obtained for pure dispersant solutions of varying concentration.

Rheological measurements were conducted on $BaTiO_3$ suspensions of varying composition using a controlled-stress rheometer (Model Rheolgi CS-50, Bohlin, Cranbury, NJ) fitted with concentric cylinder geometry. A specially designed solvent trap was used to minimize the evaporation of water. To ensure reproducibility of the data, suspensions were presheared at a shear rate of 200 s^{-1} for 30 s and then allowed to equilibrate for 300 s before the measurement was begun. Stress viscometry measurements were conducted by logarithmically ramping an applied shear stress from 0.025 to 50 Pa. A delay time (the time between two consecutive data acquisition events) of 1 min was used in this study. All rheological measurements were performed at a constant temperature of 22°C.

III. Results and Discussion

(1) PAA and PAA–PEO Solution Behavior

The ionization behavior of PAA and PAA–PEO in dilute solution was nearly identical and depended strongly on solution pH. A plot of the fraction of ionized carboxylic acid groups, α, as a function of solution pH is shown in Fig. 2, where $\alpha = [COO^-]/([COO^-] + [COOH])$. At pH 3, there were no ionized groups ($\alpha = 0$). α increased with increasing pH until complete ionization ($\alpha = 1$) was achieved at pH 9. As the PAA backbone undergoes ionization, repulsive electrostatic interactions between like-charged segments induce conformational changes in solution.

R_H of fully ionized PAA and PAA–PEO as a function of added salt is shown in Fig. 3(a). To facilitate direct comparison between mono- and divalent salt additions, the data are plotted verses the ratio $[I]/[COO^-]$, where $[I]$, the ionic strength, is given by $\frac{1}{2}\sum_i n_i z_i^2$;

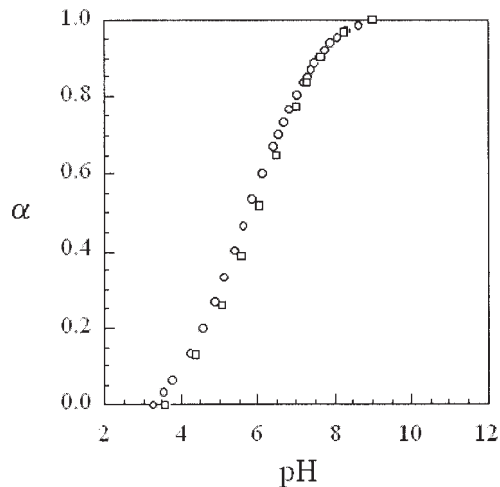**Fig. 2.** Fraction of ionized carboxylic acid groups, α, versus pH for dilute PAA (○) and PAA–PEO (□) solutions.

n_i and z_i are the molar concentration and valency, respectively, of ions "i" dissolved from the added salt species, and [COO$^-$] is the molar concentration of ionized carboxylic acid groups along the PAA backbone. The molar concentration of COO$^-$ groups was determined to be 71 and 11 mM for the PAA and PAA–PEO solutions, respectively. R_H values of 4.7 and 7.7 nm were observed for PAA and PAA–PEO, respectively, in the absence of added salt. Interestingly, R_H for PAA is only slightly less than that observed for PAA–PEO under these conditions despite significant differences in their weight-average molecular weight. On adding either mono- or divalent salt species to pure PAA solutions, R_H decreased rapidly from 6.8 nm to roughly 2 nm at [I]/[COO$^-$] $\sim$ 0.15, which corresponds to salt concentrations of 10.8 mM KCl and 3.6 mM BaCl$_2$. On further salt addition, however, the R_H of PAA remained nearly constant. This dramatic size decrease reflects a change in conformation from a highly extended chain at low ionic strength to a collapsed coil at high ionic strength. This collapse, driven by counterion interactions,[7,20] reflects the reduced intersegment repulsion between screened COO$^-$ groups along the PAA backbone. In sharp contrast, the PAA–PEO species exhibited only a slight decrease in R_H with increasing ionic strength. The relative insensitivity of PAA–PEO conformation on ionic strength likely arises due to the presence of neutral PEO teeth attached at frequent intervals along the PAA backbone. These teeth likely restrict conformational changes due to steric hindrance effects. Note, however, that the extent to which internal rearrangements of the PAA backbone are suppressed is not fully known as some conformational changes may occur that do not lead to dramatic changes in R_H.

One can estimate the R_H value for PAA in dilute solution using the following equation:[21]

$$R_H \text{ (nm)} = 0.06(\text{MW})^{0.5} \tag{1}$$

where MW is the weight-average molecular weight of the polymer. Because this expression was derived for uncharged polymers under theta solvent conditions, it represents a conservative size estimate for PAA in its fully ionized state. We have estimated the R_H value for PAA–PEO comb polymers using a modified form of the above equation:

$$R_H = 0.06(\text{MW}_{PAA})^{0.5} + 0.06(\text{MW}_{PEO})^{0.5} \tag{2}$$

where contributions from the PAA backbone and PEO teeth are accounted for by summing their individual R_H values. These calculations predict R_H values of 4.2 and 6.9 nm for PAA and PAA–PEO, respectively, which lie below the experimentally determined values, but nonetheless serve as reasonable approximations.
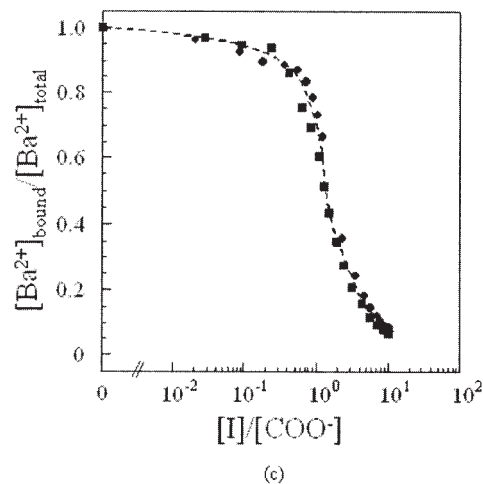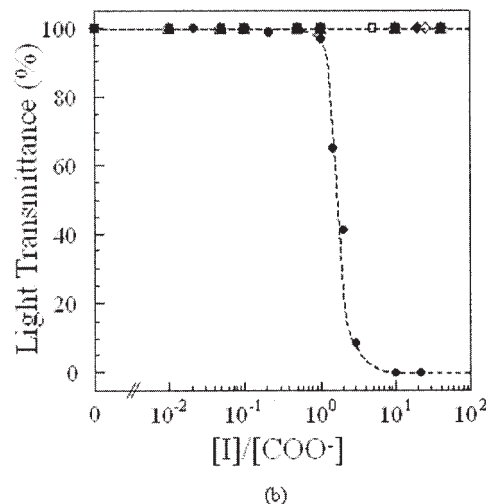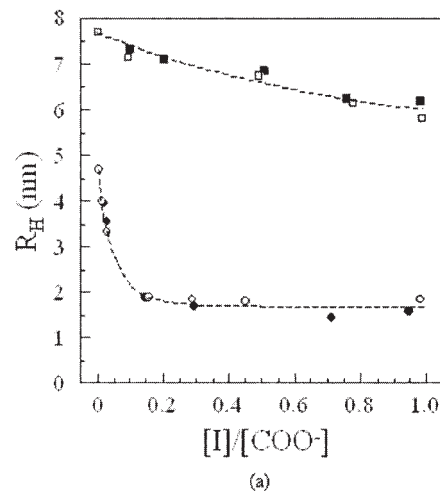

Fig. 3. Plots of the (a) hydrodynamic radius, (b) % light transmittance, and (c) fraction of bound Ba^{2+} ions as a function of salt addition for dilute solutions (c = 5 mg/mL) of PAA, pH 9 (○, ●); PAA, pH 3 (△, ▲); PAA–PEO, pH 3 (◇, ◆); and PAA–PEO, pH 9 (□, ■). Open and closed symbols correspond to KCl and BaCl$_2$ salt additions, respectively. The ratio [I]/[COO$^-$] is given by [I] $= \frac{1}{2}\sum n_i z_i^2$ due to added salt only and [COO$^-$] = 71 and 11 mM for PAA and PAA–PEO, respectively. (Note, the dashed lines merely guide the eye.)

Turbidity measurements were conducted on dilute PAA and PAA–PEO solutions as a function of varying pH and salt addition. A plot of transmitted light as a function of the ratio [I]/[COO$^-$] is shown in Fig. 3(b) for each polymer solution. Stable solutions, in

which the polymeric species remain well-solvated, are transparent (i.e., 100% light transmission). Their turbidity increases as the solution stability decreases, as reflected by a decrease in the percent of transmitted light. In the presence of monovalent salt additions ([KCl] = 0–2.8M), both PAA and PAA–PEO solutions remained transparent (stable) over a broad range of [I]/[COO$^-$] values. However, in the presence of divalent salt additions marked differences were observed between PAA and PAA–PEO solutions. The stability of pure PAA solutions depended strongly on pH and BaCl$_2$ concentration. Negligibly ionized PAA solutions remained transparent (stable) over a broad range of [I]/[COO$^-$] values, i.e., 0–1M BaCl$_2$. This is in sharp contrast to fully ionized conditions where PAA solutions were only stable over a narrow range of [I]/[COO$^-$] values, i.e., 0–3.6 mM BaCl$_2$. At higher divalent salt concentrations, the solutions became turbid due to aggregate formation; i.e., PAA chains were condensed by Ba^{2+} counterions in solution.[5] Unlike PAA, PAA–PEO solutions remained transparent (stable) over a broad range of pH conditions as well as mono- or divalent salt additions. There was no evidence of aggregation in these systems.

Remarkable differences in solution stability were observed for PAA solutions in the presence of mono- and divalent counterions under high ionic strength conditions. Unlike monovalent counterions that can only "screen" the negatively charged COO$^-$ groups along the PAA backbone, divalent ions can also promote aggregation of PAA chains in solution through "ion-bridging."[4,8,10,22] The fraction of bound divalent ions (Ba^{2+}) was characterized for dilute PAA and PAA–PEO solutions under fully ionized conditions using ion-selective electrode analysis. The molar fraction of bound Ba^{2+} ions to total Ba^{2+} ions, [Ba^{2+}]$_{bound}$/[Ba^{2+}]$_{total}$, plotted in Fig. 3(c) as a function of the ratio [I]/[COO$^-$] is nearly identical for PAA and PAA–PEO. At low BaCl$_2$ concentrations (0–3.6 mM), nearly all the divalent Ba^{2+} ions in solution are bound to PAA. On increasing the BaCl$_2$ concentration, [Ba^{2+}]$_{bound}$/[Ba^{2+}]$_{total}$ decreased until less than 10% of the total Ba^{2+} ions were bound, with the remaining ions free in solution. While the presence of PEO teeth did not significantly alter the fraction of Ba^{2+} bound to the PAA side groups, they clearly prevented ion-bridging effects from inducing aggregation, as reflected by transparent (stable) solutions over the entire range of [I]/[COO$^-$] ratios studied in the system.

(2) PAA and PAA–PEO Effects on Suspension Stability

The adsorption isotherms for PAA and PAA–PEO on BaTiO$_3$ nanoparticles suspended in solutions of varying polymer concentration ar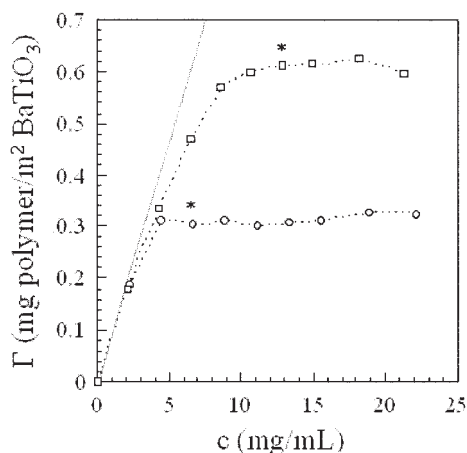e shown in Fig. 4. The adsorbed amount reached a plateau value (Γ_p) of 0.3 mg of PAA/(m^2 of BaTiO$_3$) and 0.6 mg of PAA–PEO/(m^2 of BaTiO$_3$) at a critical polymer concentration in solution (c^*) of 6.7 and 13 mg/mL for PAA and PAA–PEO solutions, respectively. Note, these values coincided with the observed transition from shear-thinning to Newtonian flow behavior indicative that stabilization was achieved at c^* (data not shown).[15]

The relative viscosities (η_{rel}) of BaTiO$_3$ suspensions are plotted in Fig. 5 as a function of the effective colloids volume fraction (ϕ_{eff}), where $\eta_{rel} = \eta_{susp}/\eta_{sol}$, η_{susp} is the apparent suspension viscosity measured in the high-shear limit, and η_{sol} is the solution viscosity. ϕ_{eff} was determined using the following relationship:[23]

$$\phi_{eff} = \phi(1 + \delta A_s \rho_s) \tag{3}$$

where δ is the thickness of the adsorbed dispersant layer (or adlayer), A_s is the specific surface area of the ceramic powder, and ρ_s is the powder density. Equation (3) accounts for excluded volume effects arising from adsorbed dispersant species, which become significant as the δ/a ratio increases. Assuming $\delta \approx R_H$, ϕ_{eff} was estimated using both calculated and experimental values of R_H, as shown in Table I. In either case, the estimated ϕ_{eff} values exhibit excellent agreement with the predicted behavior determined by the Krieger–Dougherty relationship:[24]

$$\eta_{rel} = \left(1 - \frac{\phi}{\phi_{max}}\right)^{-k\phi_{max}} \tag{4}$$

where ϕ is the colloid volume fraction and is given by ϕ_{eff} for dispersant-stabilized suspensions, $\phi_{max} = 0.63$, and k is a constant (=2.5). We therefore conclude that these δ values represent a reasonable approximation for both the PAA and PAA–PEO adlayer thicknesses.

The apparent viscosity as a function of applied shear stress was measured for BaTiO$_3$ suspensions with varying salt addition. The low-shear apparent viscosity is plotted as a function of the ratio [I]/[COO$^-$] in Fig. 6. BaTiO$_3$–PAA suspensions were stable, and exhibited nearly Newtonian flow behavior, for [I]/[COO$^-$] < 0.4, which corresponds to salt concentrations less than 36 mM KCl or 12 mM BaCl$_2$. These values are equivalent to the critical coagulation (salt) concentration required to induce shear-thinning behavior. Analogous to the polymer solution behavior, BaTiO$_3$–PAA suspensions flocculated to a much greater extent in the presence of divalent versus monovalent salt additions even under identical ionic strength conditions. In sharp contrast, BaTiO$_3$–PAA–PEO

Fig. 4. Adsorption behavior of PAA (○) and PAA–PEO (□) onto BaTiO$_3$ nanoparticles in suspension ($\phi = 0.1$, pH 9). The gray line denotes 100% adsorption. The asterisks indicate the respective critical concentrations, c^*, needed to impart full stabilization as determined by rheological measurements. (Note, the dashed lines merely guide the eye.)
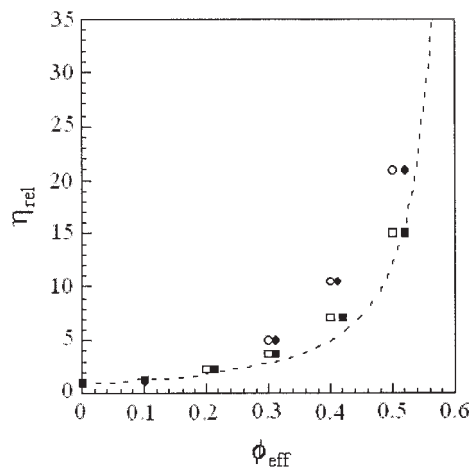
Fig. 5. Relative (high-shear) viscosity as a function of the effective solids volume fraction for BaTiO$_3$ suspensions stabilized with PAA (○, ●) and PAA–PEO (□, ■). Open and closed symbols reflect the effective volume fraction predicted using calculated and experimental values of R_H, respectively. The dashed line corresponds to theoretical behavior predicted by the Krieger–Doherty model, where $\phi_{max} = 0.63$.

Table I. PAA and PAA–PEO Effects on BaTiO$_3$ Volume Fraction in Suspension[†]

	Γ_p (mg/m^2)	R_H (nm)[‡]	Calculated R_H (nm)	ϕ	Experimental ϕ_{eff}	Calculated ϕ_{eff}
PAA	0.3	4.7	4.2	0.071	0.10	0.10
				0.142	0.21	0.20
				0.213	0.31	0.30
				0.284	0.41	0.40
				0.355	0.52	0.50
PAA–PEO	0.6	7.7	6.9	0.06	0.10	0.10
				0.12	0.21	0.20
				0.18	0.31	0.30
				0.24	0.42	0.40
				0.3	0.52	0.50

[†]pH 9, no added salt. [‡]Determined by dynamic light scattering.

suspensions exhibited stability (i.e., nearly Newtonian flow behavior) over a wide range of KCl and BaCl$_2$ concentrations, where PAA dispersants failed. In fact, we were unable to determine critical coagulation concentrations for either salt species in this system.

The apparent viscosity as a function of applied shear stress for BaTiO$_3$ suspensions of varying pH is plotted in Fig. 7. Under fully ionized conditions (pH 9), both BaTiO$_3$–PAA and BaTiO$_3$–PAA–PEO suspensions were stable, as indicated by their nearly Newtonian flow behavior. On reducing pH, the BaTiO$_3$–PAA suspensions became unstable, as reflected by an increase in their low-shear viscosity and the degree of shear-thinning behavior. In sharp contrast, BaTiO$_3$–PAA–PEO suspensions were stable over the entire pH range investigated.

Similar to the observed solution behavior, the presence of charge-neutral PEO teeth grafted at random intervals along the PAA backbone has been shown to provide stability to BaTiO$_3$ nanoparticle suspensions over a broad range of pH and ionic strength conditions where pure PAA fails. The PEO teeth provide two important functions. First, the effective size (R_H) of PAA–PEO comb polymers in solution or on ceramic particle surfaces is not significantly altered in response to variations in pH or ionic strength in their presence.[10,25–30] Second, the PEO teeth shield the underlying PAA backbone from undergoing ion-bridging interactions that lead to rapid aggregation of pure PAA molecules in solution as well as PAA-stabilized ceramic particles (see Fig. 8).

In a related study, Laarz and Bergström[31] explored the effects of PMAA–PEO comb polymers on the stability of aqueous silicon nitride (Si$_3$N$_4$) suspensions, again using PAA as a benchmark.

Their investigation was limited to Si$_3$N$_4$ suspensions in the presence and absence of monovalent salt species (i.e., 0–0.01M). On the basis of their observations, they concluded that the presence of PEO teeth provided little additional benefit beyond that observed for PAA dispersants. While this conclusion was valid on the basis of their experimental work, it is clear from our observations that under conditions of higher ionic strength or when multivalent ions are present in solution (whether added intentionally or introduced through particle dissolution or contamination) that comb polymers consisting of a polyelectrolyte backbone with charge-neutral teeth provide important process advantages.
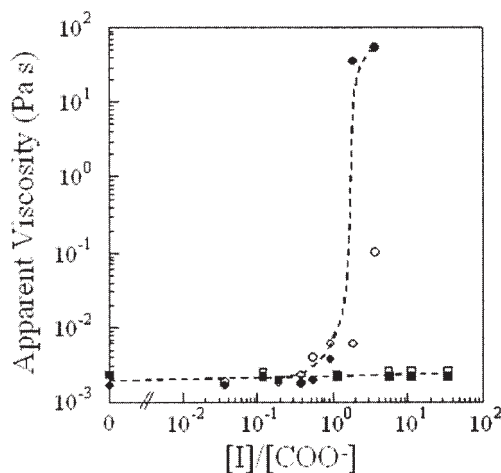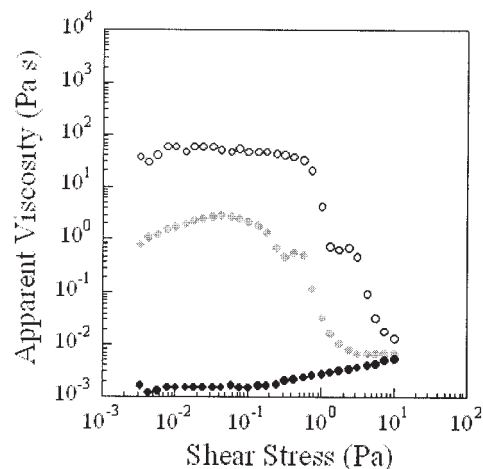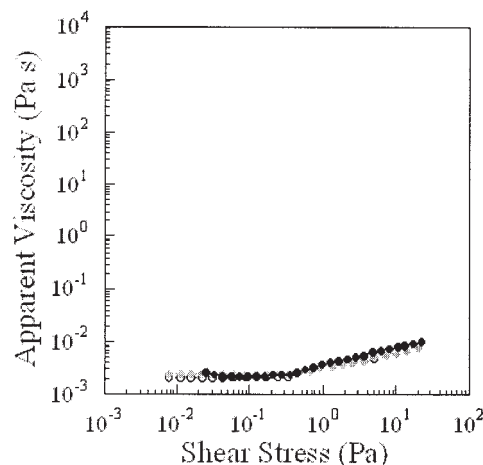
Fig. 6. Apparent viscosity ($\tau = 0.15$ Pa) as a function of salt addition for BaTiO$_3$ suspensions ($\phi = 0.1$, pH 9) with PAA (○, ●) and PAA–PEO (□, ■). Open and closed symbols reflect KCl and BaCl$_2$ salt additions, respectively. The ratio [I]/[COO$^-$] is given by [I] = $\frac{1}{2}\sum n_i z_i^2$ due to added salt only and [COO$^-$] = 90.7 and 28 mM for PAA and PAA–PEO, respectively. (Note, the dashed lines merely guide the eye.)

Fig. 7. Apparent viscosity as a function of shear stress for BaTiO$_3$ suspensions ($\phi = 0.1$) with (a) PAA and (b) PAA–PEO at pH 3 (○), pH 6 (◎), and pH 9 (●).
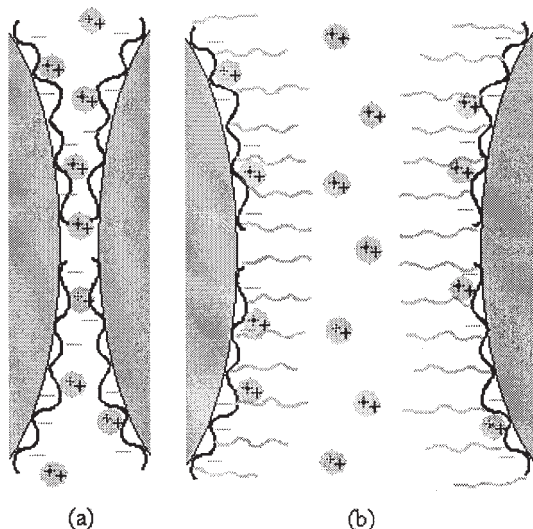
Fig. 8. Schematic illustrations of (a) flocculation between two PAA-coated ceramic particles due to divalent ion-bridging and (b) "shielding" from ion-bridging interactions provided by the PEO teeth.

IV. Conclusions

We have studied the effects of PAA–PEO comb polymer dispersants on the stability of aqueous $BaTiO_3$ nanoparticle suspensions over a broad range of pH and ionic strength conditions, using PAA as a benchmark. PAA–PEO dispersants offered far better suspension stability relative to PAA alone under analogous processing conditions. The presence of charge-neutral PEO teeth along an ionizable PAA backbone yields an electrosteric layer whose conformation is insensitive to pH or ionic strength variations. Such dispersants are expected to find widespread use in aqueous processing of ceramics.

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