Supporting Information—Electrolyte-induced Instability of Colloidal Dispersions in Nonpolar Solvents

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Synthesis of $NDod_4$-TFPhB electrolyte

The organic electrolyte tetradodecylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate ($NDod_4$-TFPhB) was obtained from a salt metathesis reaction, using a method previously developed to isolate the tetramethyl analogue.[1]

Equimolar amounts of tetradodecylammonium bromide and sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate were dissolved in methanol and combined. No precipitate was obtained as for the non-fluorinated tetraphenylborate analogues.[2] The methanol was evaporated, and the crude product redissolved in diethyl ether. The product was then washed with water three times to remove sodium bromide, and the organic layer was removed. The salt was then recrystallized from hexane/acetone, and the solvent removed to isolate the purified electrolyte. ^1H NMR spectra, ^{11}B NMR spectra, ^{19}F NMR spectra, and elemental analysis were then obtained.

^1H NMR (400 MHz, $CDCl_3$) 0.87 (12 H), 1.28 (72 H), 1.53 (8 H), 2.99 (8 H), 7.53 (4 H), 7.70 (8 H).

^{11}B NMR (128 MHz, CD_3CN, $NaBF_4$ reference) –6.55 (Aromatic BR4).

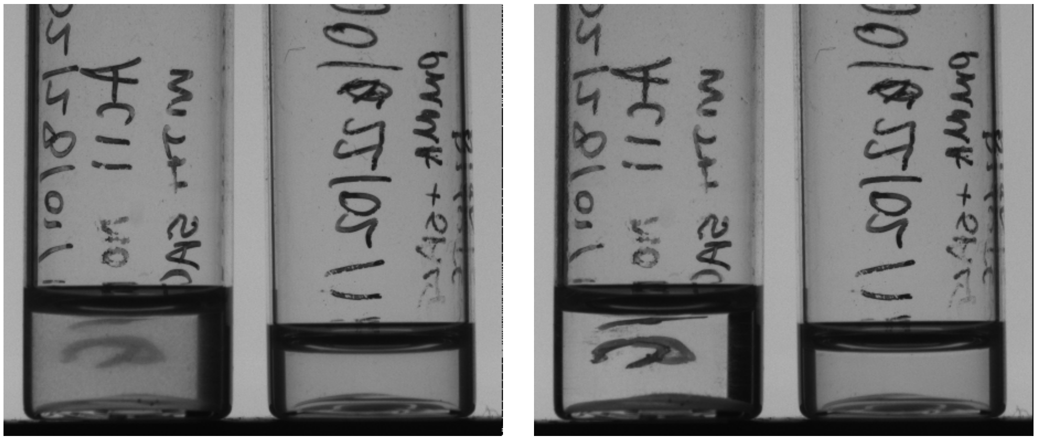
^{19}F NMR (377 MHz, $CDCl_3$, C_6F_6 reference) –65.43 (Aromatic CF_3).

Elemental analysis. Calc. for $C_{80}H_{112}BF_{24}N$: C, 61.81%; H, 7.3%; N, 0.9%. Found: C, 63.4%; H, 7.6%; N, 1.4%; Na, 0%; Br, 0.2%.

Redispersion of unstable PMMA latexes

The reversibility of the electrolyte-induced instability was studied by redispersing the destabilized dispersion of AC11 latexes into fresh dodecane. One of these samples was then centrifuged before the supernatant was removed and replaced with fresh dodecane. This process was repeated a further six times to completely remove any salt from the sample. The sample was finally made up in dodecane to match the original volume fraction and redispersed. Images were taken of the samples to compare their stability, and the redispersed sample was found to be completely stable again.

Figure S1 shows images of the latexes still in the electrolyte solution and those redispersed in fresh dodecane. The electrolyte-containing dispersion is still unstable and quickly sediments (resulting in a more transparent sample). The dispersion that had been redispersed in fresh dodecane is now stable, and there is no change in the translucency of the sample with time. This shows that the colloidal attraction is induced by the salt rather than due to an irreversible change to the latexes themselves.



(a) 0 hr

(b) 1 hr

Figure S1: Stability of destabilized AC11 latex dispersions with a high concentration of electrolyte (left) and redispersed in fresh dodecane (right). The dispersion with a high concentration of electrolyte sediments quickly, as expected from previous observations (Figure S5). The dispersion that had the electrolyte removed after redispersion in fresh dodecane is now stable. This shows that the colloidal attraction is reversible.

Electrolyte-induced instability of other PMMA latexes

Several dispersions of PMMA latexes (with different functionality and in different solvents) can be destabilized by the addition of $NDod_4$-TFPhB electrolyte. Data showing this for each of the dispersions are presented in the following subsections.

Undyed PMMA latexes in cyclohexane

MC1 latexes were provided as a gift from Merck Chemicals, Ltd. They were sized using dynamic light scattering (Malvern ZetaSizer Nano S90) and were found to have a solvodynamic diameter of 412 $\pm$ 5 nm with a polydispersity index of 0.07. They were transferred from dodecane to cyclohexane by centrifuging and redispersing five times. Dispersions in cyclohexane were prepared at a volume fraction ϕ of 5×10^{-4} and studied in solutions without electrolyte and with 3.0 mM NDod$_4$-TFPhB.

UV–visible spectra were measured over six hours, and the normalized optical density at $\lambda = 413$ nm (divided by the optical density at 0 min) is plotted as a function of time in Figure S2. The optical density of the dispersion without any electrolyte is constant (Figure S2), demonstrating that the latexes are stable, but the optical density of the dispersion in a 3.0 mM electrolyte solution decreases rapidly with time, demonstrating that the electrolyte destabilizes non-functionalized latexes in cyclohexane.

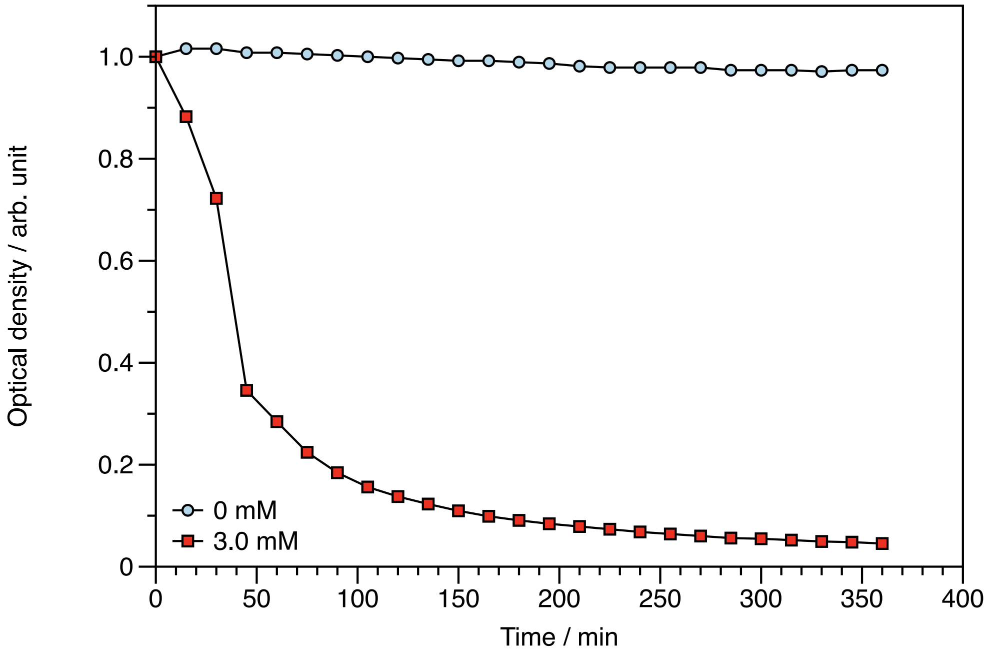
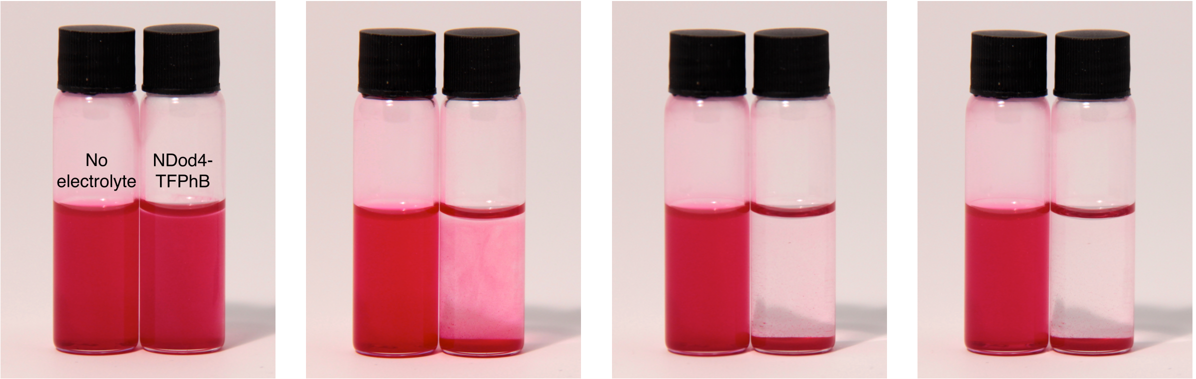


Figure S2: Normalized optical density as a function of time for non-functionalized MC1 latexes in cyclohexane both without electrolyte and in a solution of 3.0 mM NDod$_4$-TFPhB. The dispersion in electrolyte is highly unstable, shown by the decrease in the optical density.

Dyed PMMA latexes in cyclohexane

MC2 latexes were provided as a gift from Merck Chemicals, Ltd. and had a small amount of magenta dye incorporated during synthesis. They were sized using dynamic light scattering (Brookhaven ZetaPlus) and were found to have a solvodynamic diameter of 438 nm with a polydispersity index of 0.01. Dispersions in cyclohexane were prepared at a volume fraction ϕ of 5×10^{-4} and studied in solutions without electrolyte and with 3.2 mM NDod$_4$-TFPhB.

The instability of the latexes was monitored by taking images (Figure S3) of the latexes in cyclohexane with either no electrolyte or a high concentration of electrolyte. The latexes without electrolyte remain stable for at least 24 hr, whereas the latexes dispersed in an electrolyte solution begin to sediment without 1 hr.



(a) 0 hr (b) 1 hr (c) 6 hr (d) 24 hr

Figure S3: Images of dispersions of dyed MC2 latexes ($\phi = 5 \times 10^{-4}$) in a cyclohexane solution containing either no electrolyte or a high concentration of NDod$_4$-TFPhB (denoted in (a)). The dispersion without electrolyte is stable during the entire course of the observation, whereas the dispersion with added electrolyte is highly unstable.

Ionic monomer charged PMMA latexes in cyclohexane

GS4 latexes were synthesized using the Antl method[3] and had a small amount (4 wt. %) of MOTMA-TFPhB ionic monomer (**IM4** in Gillespie *et al.*[4]) incorporated during the synthesis. They were sized using dynamic light scattering (Malvern ZetaSizer Nano S90) and were found to have a solvodynamic diameter of 360. ± 2 nm with a polydispersity index of 0.09. The charge of the latexes in cyclohexane was measured using phase-analysis light scattering (Malvern ZetaSizer Z) and were found to have an electrophoretic mobility μ of $(12.4 \pm 0.6) \times 10^{-10}$ m^2 V^{-1} s^{-1}. Dispersions in cyclohexane were prepared at a volume fraction ϕ of 5×10^{-4} and studied in solutions without electrolyte and with 3.0 mM NDod$_4$-TFPhB.

UV–visible spectra were measured over six hours (shown in Figure S4), using the same method as in Figure S2. As for plain latexes, the optical density without any electrolyte is constant, and the optical density in an electrolyte solution decreases rapidly with time.

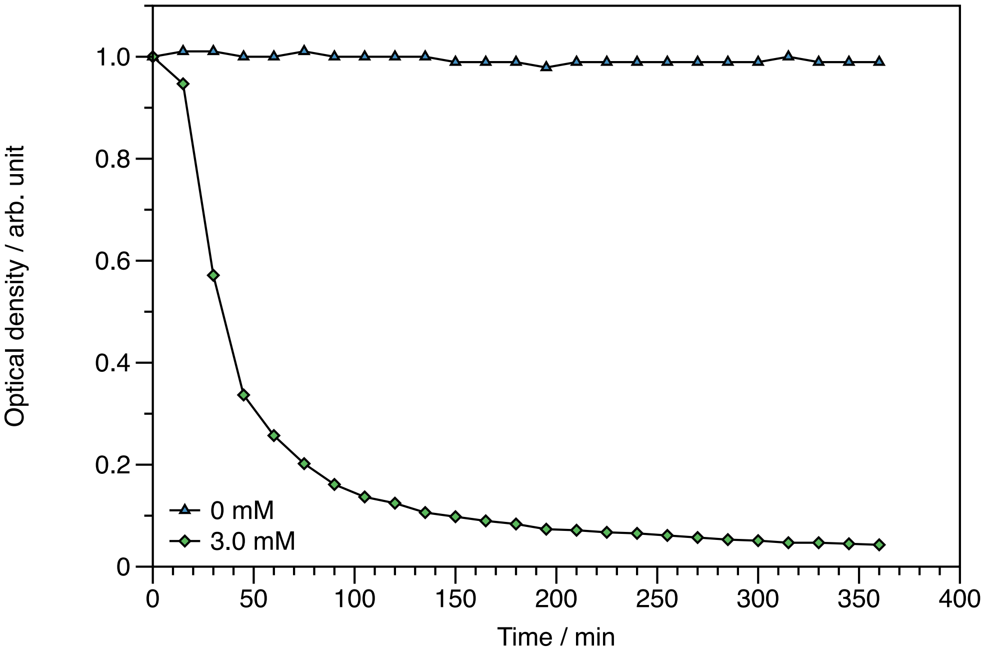
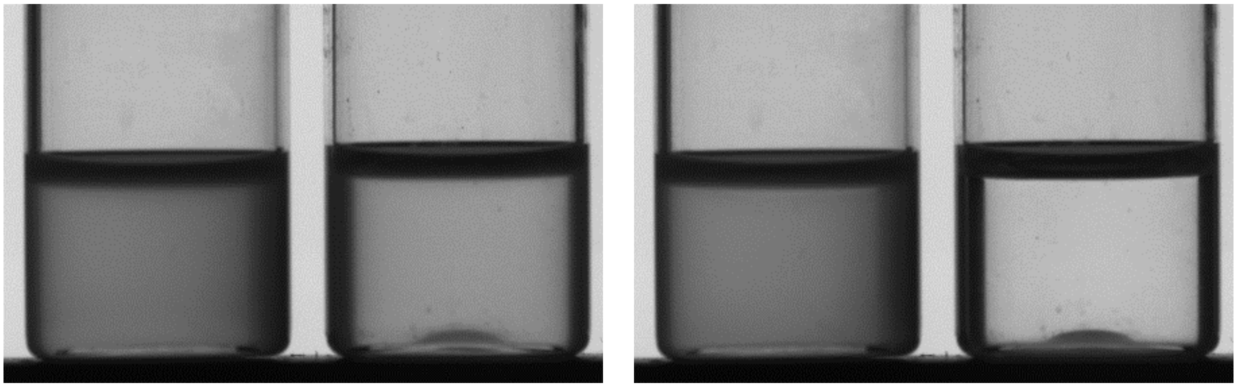


Figure S4: Normalized optical density as a function of time for ionic monomer charged GS4 latexes in cyclohexane both without electrolyte and in a solution of 3.0 mM NDod$_4$-TFPhB. The dispersion in electrolyte is highly unstable, shown by the decrease in the optical density.

Undyed PMMA latexes in dodecane

AC11 latexes were synthesized using the Antl method[3] without functionality incorporated. The particles have a diameter of 1290 ± 50 nm. Dispersions were prepared at a volume fraction ϕ of $\sim 3 \times 10^{-4}$ and studied in solutions without electrolyte and with 0.43 mM NDod$_4$-TFPhB. The instability was monitored by taking images (Figure S5) of the latexes in dodecane with either no electrolyte or a high concentration electrolyte. The dispersion without electrolyte is stable over 1 hr, whereas the latexes dispersed in the electrolyte solution sediment entirely over the 1 hr long observation.



(a) $t = 0$ (b) $t = 1$ hr

Figure S5: Images of dispersions of non-functionalized AC11 latexes in an dodecane solution containing either no electrolyte (left) or a high concentration of NDod$_4$-TFPhB (right). The dispersion without electrolyte is stable during the entire course of the observation, whereas the dispersion with added electrolyte is highly unstable.

Ionic monomer charged PMMA latexes in dodecane

PIL latexes were synthesized using the Antl method[3] and had a small amount (2 wt. %) of ILMC$_{12}$-TFPhB ionic monomer (**IM2** in Gillespie *et al.*[4]) incorporated during the synthesis. They were sized using dynamic light scattering (Malvern ZetaSizer Nano S90) and were found to have a solvodynamic diameter of 1020 ± 20. Dispersions in dodecane were prepared at a volume fraction of ϕ of 1.17×10^{-3} and studied in solutions with out electrolyte and with 0.3 mM NDod$_4$-TFPhB.

The instability was monitored by taking images (Figure S6) of the latexes in dodecane with either no electrolyte or a high concentration of electrolyte. Dispersions were immediately destabilized in electrolyte solutions, and this made it impossible to take an image before sedimentation occurred. The latexes were clearly aggregating by eye, however.

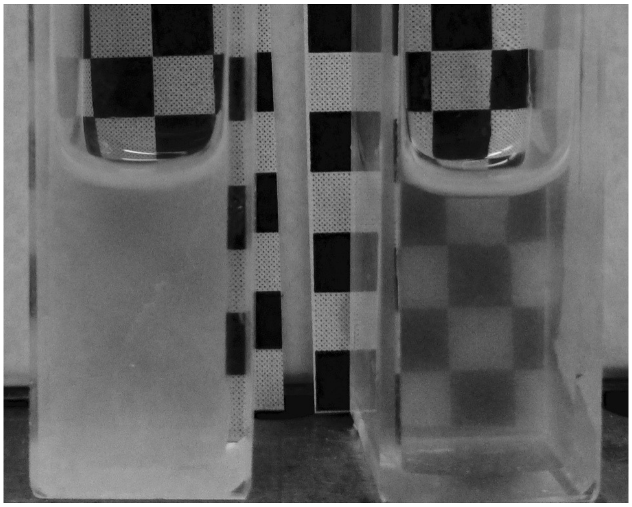


Figure S6: Image of dispersions of ionic monomer-functionalized PIL latexes in an dodecane solution containing either no electrolyte (left) or a high concentration of NDod$_4$-TFPhB (right). The dispersion without electrolyte is entirely stable, whereas the dispersion in the presence of electrolyte is highly unstable, immediately beginning to aggregate and sediment.

Blinking optical tweezers

By "blinking" (interrupting) the trapping laser beam, the particles are allowed to move freely for a short period of time (25 ms) before being trapped and returned to their initial separation. This was achieved by use of a beam chopper (Thorlabs MC2000) interrupting a $\lambda = 1024$ nm laser. The laser beam is focused through a high numerical aperture objective (Zeiss Plan-Neofluar, 100×, 1.3 N.A.) after reflection from a spatial light modulator (SLM, Holoeye PLUTO-NIR). This SLM, controlled by software from the Glasgow Optics Group[5] determines the positions and numbers of optical traps. Finally, a high speed camera (Dalsa Genie HM640) took images of the particles at 500 Hz.

In an overdamped system, the particle velocity (v) is directly proportional to the force (F) acting on it: $v = b \cdot F$, where b is the coefficient of friction. The particles are positioned at an initial separation, and 5000 blinking events are measured. These data are processed to calculate the force. The gradient of the mean displacement with time gives the velocity, while the gradient of the variance as a function of time gives the diffusion coefficient. Equation S1, where r is the initial particle separation, is used to calculate the interparticle force ($F(r)$).

$$F(r) = \frac{k_B T}{D} v \tag{S1}$$

Charge of undyed PMMA latexes in dodecane

A force-distance curve was measured for AC11 particles to ensure the dye played no significant role in the loss of stability. The resulting data shows that the undyed particles have a charge of 78 ± 1 e and can be fit using a purely Coulombic repulsion. This compares well to the charge of the AC12 latexes ($Z = 56 \pm 1$ e).

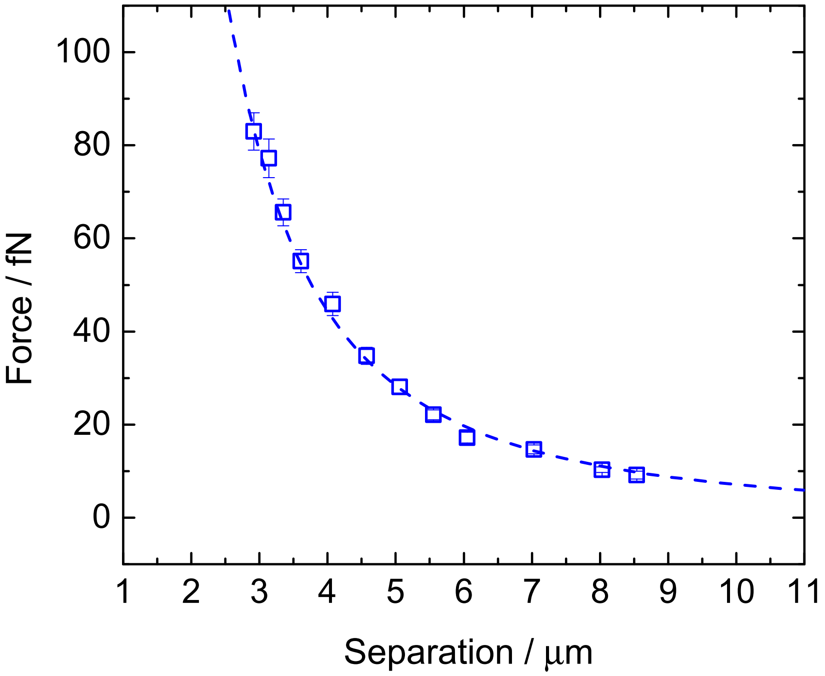


Figure S7: Interaction forces between AC11 latexes with no added salt, measured by the blinking tweezers technique. The data are fit to the Yukawa Force equation given in the Letter (dashed lines) and show that the undyed particles interact with an unscreened interaction ($Z = 78 \pm 1$ e).

Electrical conductivity of $NDod_4$-TFPhB solutions in dodecane

The electrical conductivity of solutions of $NDod_4$-TFPhB in dodecane for concentrations from 5–80 μM was measured using a model 627 conductivity meter (Scientifica, Princeton, NJ). The measured molar conductivity (Λ) values are shown in Figure S8. The data have been analyzed using Fuoss–Krauss theory, which describes the molar conductivity as a sum of single and triple ions with associated dissociation constants.[6]

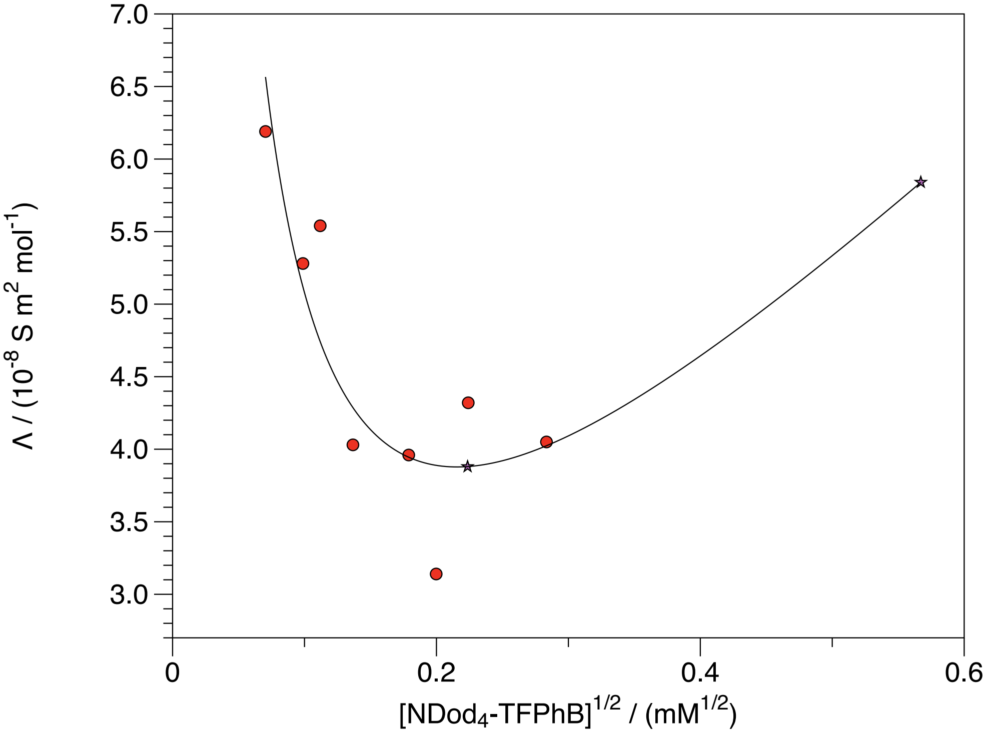


Figure S8: Molar conductivity (Λ) of $NDod_4$-TFPhB in dodecane. The red circles show the measured data, and the purple stars show extrapolated values of Λ for the electrolyte solutions used in this study.

Small-angle neutron scattering (SANS)

Neutron scattering measurements were performed on the instrument Sans2d at the ISIS Pulsed Neutron Source (STFC Rutherford Appleton Laboratory, Didcot, UK).[7] Raw scattering data sets were corrected for the detector efficiency, sample transmission, and background scattering and converted to scattering cross sections using the instrument-specific software Mantid.[8,9] These data were placed on an absolute scale (cm^{-1}) using the scattering from a standard sample (a solid blend of hydrogenous and perdeuterated polystyrene).[10]

SANS data were obtained for three samples: a solution of PMMA-*graft*-PHSA stabilizer copolymer in dodecane (2 wt. %), a solution of $\mathrm{NDod_4}$-TFPhB (concentration of 0.46 mM), and a mixture of the two. Deuterated dodecane-d_{26} was used to dilute the stabilizer copolymer concentrate and dissolve the $\mathrm{NDod_4}$-TFPhB to obtain isotopic contrast for SANS experiments. It has been previously shown that the stabilizer polymer aggregates into elongated polymer micelles when dissolved in alkanes, good solvents for the PHSA grafts but bad solvents for the PMMA backbone.[11,12] Tetraalkylammonium borate salts are know to self-assemble into small clusters in aliphatic hydrocarbon solvents.[13] By comparing these three scattering curves, it is possible to work out whether the small molecule solute disrupts the polymer micelles, as was previously done for mixtures of AOT-d_{34} and PMMA-*graft*-PHSA.[12] SANS data are shown in Figure S9.

The scattering curves from the two polymer samples are essentially identical, showing that the electrolyte does not disrupt the structure of the polymer micelles. This polymer micelles, which presumably form with PMMA blocks in the interior and PHSA brushes extending in the solvent, are a good model for the PMMA latex surface. There would be insufficient contrast to study the conformation of the PHSA brushes on the surface of the latexes themselves. These data show that the two solutes (PMMA-*graft*-PHSA and $\mathrm{NDod_4}$-TFPhB) do not interact, and therefore, the possible explanation that the latexes could be destabilized by the electrolyte making PHSA an ineffective steric stabilizer cannot explain the observed instability of the latexes.

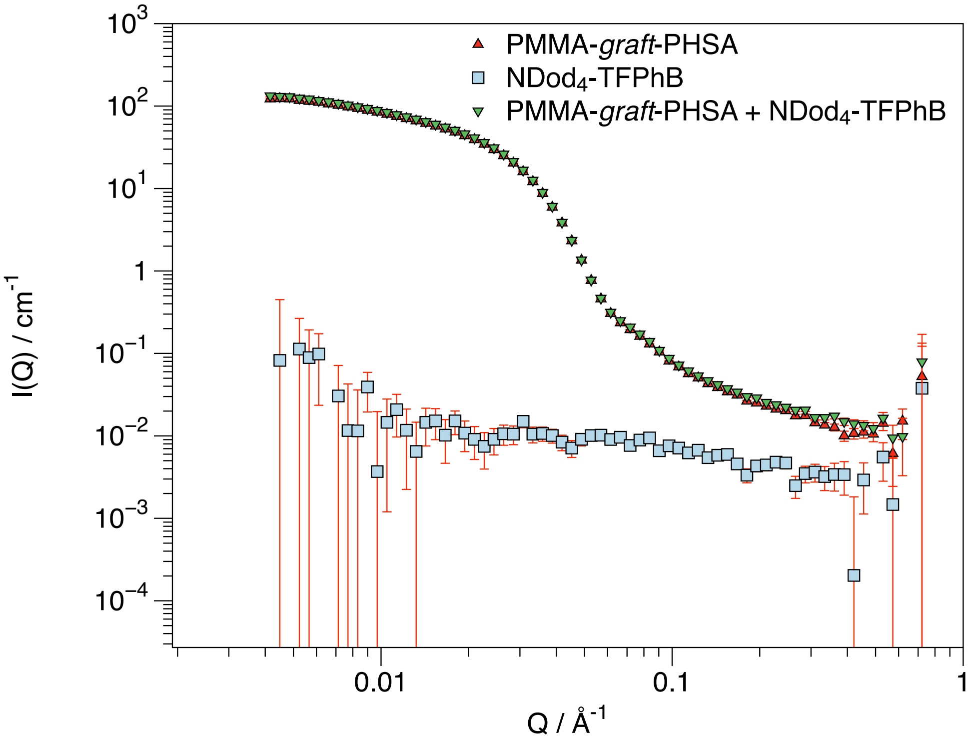


Figure S9: SANS curves for PMMA-*graft*-PHSA and NDod$_4$-TFPhB in dodecane-d_{26}. The scattering from the polymer micelles is as expected from literature,[12] dwarfing the scattering from the NDod$_4$-TFPhB clusters.

References

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