

# Polymer Conductivity through Particle Connectivity

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## Supporting Information

PAAMPSA was synthesized via conventional free-radical polymerization while aPAAMPSA was synthesized by atom transfer radical polymerization,<sup>S1, S2</sup> and they were subsequently used to template polymerize aniline. The details of PAAMPSA (and aPAAMPSA) synthesis, along with those of PANI-PAAMPSA (and PANI-aPAAMPSA) template synthesis have been detailed elsewhere.<sup>S3, S4</sup> In this report, PANI-PAAMPSA-X denotes PANI that we had template synthesized on PAAMPSA whose poly(ethylene oxide) equivalent number-average molecular weight in kg/mol is X. Given that the underlying PAAMPSA was made by conventional free-radical polymerization, PAAMPSA generally has a broad molecular weight distribution. The molecular weight distribution of PAAMPSA is characterized by the polydispersity index ( $PDI = M_w/M_n$ ); a PDI of 1 indicates a monodisperse sample whereas a PDI of 2 indicates that the polymer has the most probably chain length distribution.<sup>S3</sup> Another series of conductive polymer, PANI-aPAAMPSA-X, was synthesized using aPAAMPSA that was derived from atom transfer radical polymerization. Consequently, the polymer acid template generally has a narrower molecular weight distribution compared to those synthesized by conventional free-radical polymerization, characterized by a smaller PDI. The relevant chemical and physical characteristics of all the PANI-PAAMPSA (and PANI-aPAAMPSA) specimens examined in this study are detailed in Table S1.

The size and number-weighted size distribution of PANI-PAAMPSA (and PANI-aPAAMPSA) particles were quantified by dynamic light scattering (DLS). All the DLS experiments were performed on 0.0001 wt% PANI-PAAMPSA (or PANI-aPAAMPSA) in 0.1 M NaCl aqueous solutions to effectively screen interparticle electrostatic

interactions. This salt concentration was selected after a series of experiments carried out at varying salt concentrations.<sup>S5</sup> Figure S1a details the mean hydrodynamic diameter of PANI-PAAMPSA-724 extracted from 0.0001 wt% polymer dispersions at varying salt concentrations. We observe that the mean hydrodynamic diameter starts out high at low salt concentrations, and plateaus at NaCl concentrations above  $10^{-2}$  M. This observation suggests that a salt concentration of at least  $10^{-2}$  M is required to prevent aggregation of PANI-PAAMPSA (and PANI-aPAAMPSA) particles. Above  $10^{-2}$  M NaCl concentration, the mean hydrodynamic diameter extracted from DLS represents that of individually isolated particles. This quantity is consistent with the average size of the particles extracted from TEM (see Figure 3). We have therefore opted to keep the salt concentration at 0.1M NaCl for all our DLS experiments. Figure S1b shows how the mean hydrodynamic diameter of PANI-PAAMPSA-724 changes with increasing polymer concentration at a constant salt concentration of 0.1 M NaCl. Below a polymer concentration of 0.001 wt%, the hydrodynamic diameter is independent of polymer concentration, suggesting that this value is that of individual isolated particles. Above 0.001 wt%, however, aggregation occurs so the mean hydrodynamic diameter extracted from DLS increases accordingly. All DLS experiments were performed at conditions at which interparticle electrostatic interactions are effectively screened (0.0001 wt% polymer in 0.1M NaCl solution).

We account for the packing of the particles in the film by considering them to interact as hard spheres with the experimentally determined size distribution, scaled in each system to yield approximately 2000 particles. We simulate the “concentration” of this hard-sphere system using the Lubachevsky-Stillinger algorithm.<sup>S6</sup> In this method, event-

driven molecular dynamics for the particles is carried out in a periodically-replicated simulation cell.<sup>S7</sup> The simulation cell volume is kept constant while the radius of the  $j$ th particle  $r_j(t)$  is allowed to “grow” linearly in time  $t$  according to:

$$r_j(t) = r_j(0) + \Gamma \frac{r_j(0)}{\langle r_j(0) \rangle} \sqrt{\frac{k_B T}{m}} t \quad (\text{S1})$$

where  $\langle r_j(0) \rangle$  is the average initial particle radius,  $\Gamma$  is a dimensionless growth rate,  $T$  is the temperature,  $k_B$  is the Boltzmann constant, and  $m$  is the particle mass. For completeness, we simulated  $\Gamma = 0.05, 0.005, 0.001$  and  $0.0001$ , which covers a very wide range of effective “concentration” rates known to produce amorphous packings. The system is considered jammed when the packing can no longer accommodate further particle growth (relative to the cell dimension), which is determined by a very small change in sphere size,  $\Delta d$ , from one collision step to the next:

$$\Delta d = \frac{1}{N_c} \sum_{k=2}^{N_c} \frac{r^{\max}(t_k) - r^{\max}(t_{k-1})}{r^{\max}(t_k)} \quad (\text{S2})$$

Here  $r^{\max}(t_k)$  and  $r^{\max}(t_{k-1})$  are the radii of the largest sphere at the  $k$ th and  $(k-1)$ th collision, and  $N_c$  is the number of collisions used to calculate  $\Delta d$ . In this work, we used  $N_c = 10^4$  and consider the system jammed when  $\Delta d \leq 5 \times 10^{-9}$ . To obtain the distribution of particle diameters for the simulation at each state point, we scaled the experimental intensities such that the total number of particles was approximately 2000. The

Lubachevksy-Stillinger compressions were initialized from equilibrated hard-sphere fluid configurations at a packing fraction of  $\phi = 0.3$ . For each particle-size distribution and growth rate  $\Gamma$ , we created 30 independent randomly jammed configurations. The average jammed packing fractions of these systems  $\phi_i$  are presented in Table S2. Note that the final  $\phi_i$  varies by at most a few percent over a wide range of particle-size distributions and effective concentration rates, especially when compared to the large differences in film conductivity. This result implies that one can accurately estimate the particle number density,  $\rho_i$ , or alternatively, the final particle surface area per film volume for each experiment,  $A_i/V$ , given the experimental particle-size distribution and assuming that all systems have the same  $\phi_i$ . To illustrate this point, we considered the particle surface area per film volume for each system to be given by:

$$A_i/V = \phi_i \frac{3\langle r^2 \rangle}{\langle r^3 \rangle} \quad (\text{S3})$$

where  $\phi_i$  is the packing fraction obtained from simulation, and the quantities  $\langle r^2 \rangle$  and  $\langle r^3 \rangle$  are the experimentally determined second and third moments, respectively, of the particle radius distribution. In Figure S2, we plotted this quantity as a function of  $A(\phi = 0.64)/V$ , which assumes that all films have the same  $\phi$  of 0.64.<sup>S8, S9</sup> As the figure illustrates, the results are insensitive to the assumption that the  $\phi$  is constant.

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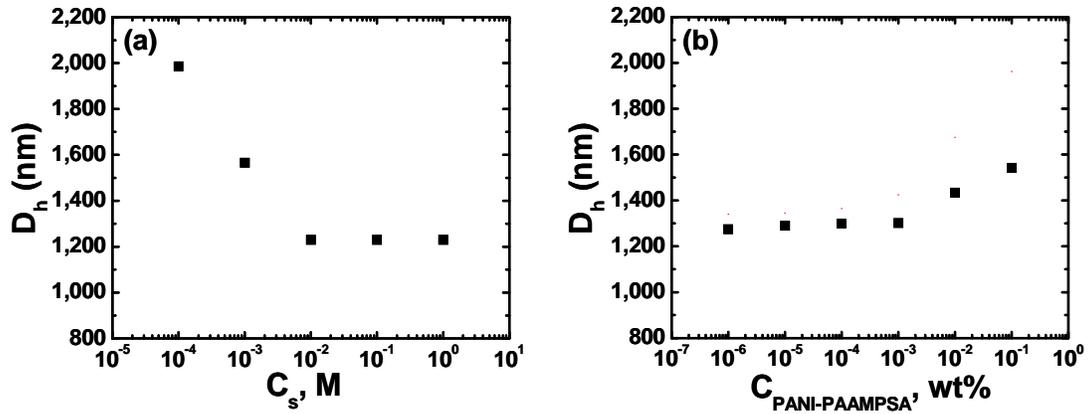
**Table S1.** Physical characteristics of the PAAMPSAs (and aPAAMPSAs) that are used to dope PANI, and those of the corresponding PANI-PAAMPSA (or PANI-aPAAMPSA).

Nomenclature	$M_n$ [a] of PAAMPSA (aPAAMPSA) [kg/mol]	PDI of PAAMPSA (aPAAMPSA)	Conductivity [S/cm]	$D_h$ of particles [c] [nm]	FWHM [b] particle-size distribution [c] [nm]
PANI-PAAMPSA- 45	45	1.43	$1.09 \pm 0.03$	$543 \pm 9$	$636 \pm 12$
PANI-PAAMPSA- 83	83	1.53	$0.82 \pm 0.02$	$699 \pm 17$	$671 \pm 15$
PANI-PAAMPSA- 106	106	1.53	$0.67 \pm 0.01$	$774 \pm 16$	$703 \pm 3$
PANI-PAAMPSA- 255	255	1.64	$0.55 \pm 0.02$	$908 \pm 18$	$788 \pm 13$
PANI-PAAMPSA- 724	724	1.64	$0.43 \pm 0.02$	$1232 \pm 25$	$926 \pm 69$
PANI-aPAAMPSA- 30	30	1.16	$2.39 \pm 0.03$	$560 \pm 11$	$374 \pm 5$
PANI-aPAAMPSA- 67	67	1.14	$1.95 \pm 0.11$	$626 \pm 13$	$373 \pm 4$
PANI-aPAAMPSA- 117	117	1.20	$1.52 \pm 0.12$	$739 \pm 15$	$394 \pm 9$
PANI-aPAAMPSA- 150	150	1.25	$1.32 \pm 0.05$	$782 \pm 18$	$414 \pm 9$
PANI-aPAAMPSA- 287	287	1.28	$1.07 \pm 0.03$	$820 \pm 16$	$430 \pm 15$

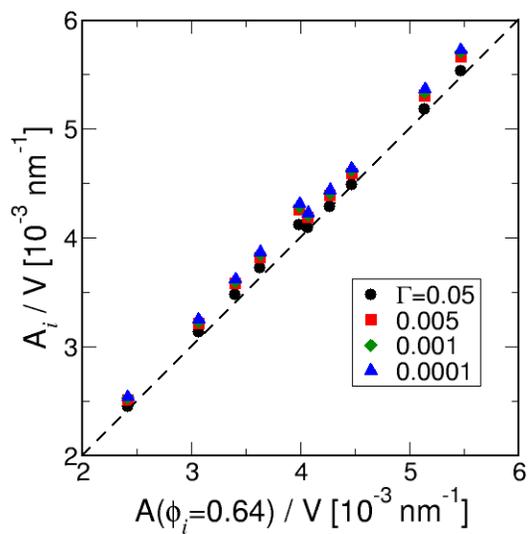
[a] PEO-equivalent  $M_n$  of PAAMPSA (or aPAAMPSA), in kg/mol. [b] The full width of the size distribution of particle acquired by DLS at half its maximum intensity. [c] Standard deviation determined from 5-7 independent runs to account for run-to-run variations.

**Table S2.** Final particle packing fractions for each system and particle growth rate.

Nomenclature	$\phi_i$			
	$\Gamma = 0.05$	$\Gamma = 0.005$	$\Gamma = 0.001$	$\Gamma = 0.0001$
PANI-PAAMPSA-45	0.662	0.684	0.689	0.692
PANI-PAAMPSA-83	0.656	0.674	0.679	0.683
PANI-PAAMPSA-106	0.654	0.673	0.677	0.681
PANI-PAAMPSA-255	0.653	0.671	0.675	0.679
PANI-PAAMPSA-724	0.649	0.666	0.669	0.673
PANI-aPAAMPSA-30	0.647	0.663	0.667	0.670
PANI-aPAAMPSA-67	0.645	0.662	0.665	0.669
PANI-aPAAMPSA-117	0.643	0.658	0.662	0.665
PANI-aPAAMPSA-150	0.643	0.658	0.662	0.665
PANI-aPAAMPSA-287	0.642	0.658	0.662	0.665



**Figure S1.** The mean hydrodynamic diameter of PANI-PAAMPSA-724 extracted from DLS experiments (a) at a constant polymer concentration of 0.0001 wt% but with increasing NaCl concentration and (b) at a constant NaCl concentration of 0.1 M but with increasing polymer concentration.



**Figure S2.** Particle surface area to film volume ratio  $A_i / V$  versus the same quantity if one assumes that  $\phi$  is 0.64,  $A(\phi_i = 0.64) / V$ . The dashed line is  $A_i / V = A(\phi_i = 0.64) / V$ .