

Supporting Information

For

# Studies of Ionic Current Rectification Using Polyethyleneimines Coated Glass Nanopipettes

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## Dynamic Light Scattering Measurements

The size of PEIs molecules, both linear and branched structures, were evaluated by dynamic light scattering (DLS), a well-established method for sizing nanomaterials.<sup>1,2</sup>

A commercialized spectrometer (Brookhaven Inc., Holtsville, NY.) was used to conduct DLS over a scattering angular range of 30–90°. A 100 mW solid-state laser (GXC-III, GNI, Changchun, China) operating at 532 nm was used as the light source.

DLS measures the intensity–intensity time correlation function  $G^{(2)}(\tau)$  in the self-beating mode, where  $\tau$  is the relaxation time.  $G^{(2)}(\tau)$  is related to the electric field time correlation function  $g^{(1)}(\tau)$  as  $G^{(2)}(\tau) = A(1 + b|g^{(1)}(\tau)|^2)$ , where  $A$  and  $b$  are the, respective measured baseline and a coherence factor. The electric field time correlation function  $g^{(1)}(\tau)$  is analyzed by the constrained regularized CONTIN method<sup>3</sup> to yield the characteristic line width distribution  $G(\Gamma)$ ,

$$|g^{(1)}(\tau)| = \int_0^\infty G(\Gamma) \exp(-\Gamma\tau) d\Gamma \quad (\text{s1})$$

where  $\Gamma$  is the characteristic line width. The average line width,  $\bar{\Gamma}$ , is calculated according to  $\bar{\Gamma} = \int \Gamma G(\Gamma) d\Gamma$ .  $\bar{\Gamma}$  is a function of both  $c$  and  $q$ , which can be expressed as

$$\bar{\Gamma} / q^2 = D(1 + k_d c) \left[ 1 + f(R_g q)^2 \right] \quad (\text{s2})$$

with  $D$ ,  $k_d$ ,  $f$  being the translational diffusive coefficient, the diffusion second virial coefficient, and a dimensionless constant, respectively.  $D$  can be further converted into the hydrodynamic radius  $R_h$  using the Stokes–Einstein equation:

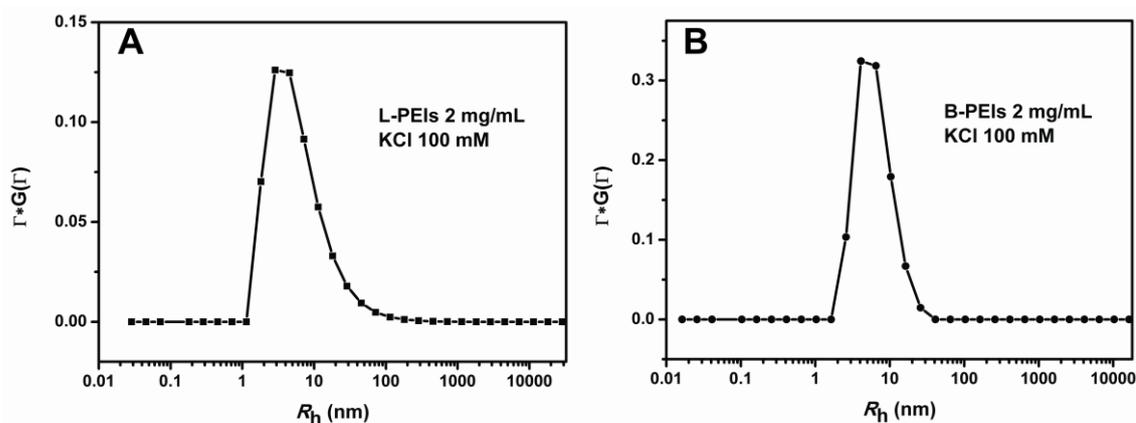
$$D = k_B T / 6\pi\eta R_h \quad (\text{s3})$$

where  $k_B$ ,  $T$ ,  $\eta$  are the Boltzmann constant, the absolute temperature, and the viscosity of the solvent, respectively.

The concentrations we used in the modification were 0.1 and 0.9 mg/mL, respectively. However, the light intensity was too weak to be detected under these concentrations. In order to obtain detectable signals, the concentration of PEIs was increased to 2 mg/mL. KCl was added into the solution to prevent the conjugations induced by high concentration of PEIs. Besides, linear PEIs were only soluble in hot water at 2 mg/mL.

So the test was carried out at 50 °C for linear PEIs.

The size distributions of PEIs are shown in Figure S1. The  $R_h$  of linear PEIs and branched PEIs at 30 ° are 4.1 nm (correlated to temperature at 22°C) and 5.3 nm, respectively. Because PEIs carry positive charges, the resulted mean hydrodynamic radius should be a little bit larger than the actual size of PEIs in the solution, which is an inherent problem of DLS. In addition, the size reported here is the radius of hydrated form of PEIs in free solutions. When PEIs were immobilized on the glass surface, they would exist in a more condensed form, which means the size should be even smaller (see Figure 2B).



**Fig. S1** Size distribution of linear PEIs (A) and branched PEIs (B).  $c(\text{PEIs}) = 2 \text{ mg/mL}$ .  $c(\text{KCl}) = 100 \text{ mM}$ . (A)  $R_h = 4.1 \text{ nm}$ . Temperature: 50 °C. (B)  $R_h = 5.3 \text{ nm}$ . Temperature: 22 °C.

The results above may help to prove that the ICR behavior after modification is not totally caused by the aggregation of large PEIs molecules with counter anions formed near the tip, but the increased positive charge densities on the surface.

## References

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