1. DLP MODEL

The complex permittivity $\varepsilon^*(\omega)$ can be derived into the contribution of countions fluctuation along chains axes $\varepsilon^*_l(\omega)$ and that perpendicular to chains axes $\varepsilon^*_h(\omega)$, respectively:

$$
\varepsilon^* = \varepsilon^*_l(\omega) + \varepsilon^*_h(\omega) + A\omega^{-m} - \frac{B\omega^{1-m}}{i\omega\varepsilon_0}
$$

(S1)

Where $\omega(=2\pi f, f$ is the measured frequency) is the angular frequency, $A\omega^{-m}$ is the electrode polarization (EP) term of the permittivity data and the corresponding $B\omega^{1-m}/i\omega\varepsilon_0$ is the electrode polarization (EP) term of the dielectric loss data. A, B and m are the empirical parameters, m is related to the electrical phase angle $\delta (=\pi(1-m)/2)$ to characterize electrode polarization.\(^{1-3}\)

According to the DLP theory of flexible polyelectrolyte,\(^4\) the contribution of low-frequency (LF) relaxation can be expressed as:

$$
\varepsilon^*_l(\omega) = \frac{\Delta\varepsilon_i}{1 + \left(-i\omega\xi^2/D_i\right)^\alpha}
$$

(S2)

where $\xi$ is the correlation length, $D_i (=k_B T M_i)$ is the diffusivity of the countions, $M_i$ is the mobility of the countions, $k_B T$ is the thermal energy, and $\alpha$ is the the distribution coefficient of low-frequency (LF) relaxation. On the basis of the perturbation calculation of PE solution, the dielectric increment can be defined as:

$$
\Delta\varepsilon_i = \frac{16\pi}{9} \varepsilon \phi \xi \left(\frac{G_i}{G_0}\right)^2
$$

(S3)

Where $\phi$ is the volume fraction of PE chains, $G_0(=M_i q^2/l_B)$ is the linear conductance of the countions in the bulk, $l_B$ is the distance at which the electrostatic interaction between two elementary charges in the medium is equal to the thermal energy $k_B T$.

The contribution of countion fluctuation along chains axis to linear conductance can be given as:

$$
G_i = M_i q \rho_i
$$

(S4)
Where the linear charged density of counterions that cause LF relaxation can be expressed as:

$$\rho_t = -2\pi \varepsilon_0 \varepsilon_i \frac{\kappa \alpha K_\alpha(\kappa \alpha)}{K_\alpha(\kappa \alpha)} \zeta$$  \hspace{1cm} (S5)

Where \(\varepsilon_0\) is vacuum dielectric constant and \(K_\alpha(\alpha=0,1)\) is the modified Bessel function, which was used to describe the distribution of electric potential around the charged cylinder.

The contribution of high-frequency (HF) relaxation can be expressed as:

$$\varepsilon_h^*(\omega) = \frac{\Delta \varepsilon_h}{1 + \left(-i\omega/\omega_h\right)^\beta}$$  \hspace{1cm} (S6)

Where \(\omega_h\) is the relaxation angular frequency and \(\beta\) is the distribution coefficient of high frequency relaxation. The dielectric increment can be defined as:

$$\Delta \varepsilon_h = \frac{2}{9\pi^2} \frac{\varphi G_h^2 \kappa}{\omega_h^2 \varepsilon_0^2 \varepsilon_i \nu}$$  \hspace{1cm} (S7)

The contribution of counterion fluctuation perpendicular to chain axes to linear conductance can be given as:

$$G_h = 2qM_i \rho_h (1 - \frac{1}{2\pi \eta l_i M_i})$$  \hspace{1cm} (S8)

Where \(\eta\) is the viscosity of the solvent, and the linear charged density of counterions that cause HF relaxation can be given as:

$$\rho_h = \frac{\pi \varepsilon_0 \varepsilon_i \varepsilon^2}{4k_B T} \left(\frac{\kappa \alpha K_\alpha(\kappa \alpha)}{K_\alpha(\kappa \alpha)}\right)^2 - \frac{\pi \varepsilon_0 \varepsilon_i \varepsilon^2 (\kappa \alpha)^2}{4k_BT}$$ \hspace{1cm} (S9)


