Electronic Supplementary Material (ESI) for Soft Matter.

1. DLP MODEL

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

$$\varepsilon^* = \varepsilon_l^*(\omega) + \varepsilon_h^*(\omega) + A\omega^{-m} - \frac{B\omega^{1-m}}{i\omega\varepsilon_0} \tag{S1}$$

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 δ $(=\pi(1-m)/2)$ 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:

$$\varepsilon_l^*(\omega) = \frac{\Delta\varepsilon_l}{1+\left(-i\omega\xi^2 / D_i\right)^{\alpha}} \tag{S2}$$

where ξ is the correlation length, Di $(=k_B T M_i)$ is the diffusivity of the counterions, M_i is the mobility of the counterions, $k_B T$ is the thermal energy, and α 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:

$$\Delta\varepsilon_l = \frac{16\pi}{9}\frac{\varepsilon_s\varphi\xi}{\nu\kappa^2}\left(\frac{G_l}{G_0}\right)^2 \tag{S3}$$

Where φ is the volume fraction of PE chains,$G_0(=M_i q^2/l_B)$ is the linear conductance of the counterions 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 counterion fluctuation along chains axis to linear conductance can be given as:

$$G_l = M_i q \rho_l \tag{S4}$$

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

$$\rho_l = -2\pi\varepsilon_0\varepsilon_s \frac{\kappa a K_1(\kappa a)}{K_0(\kappa a)}\zeta \quad \text{(S5)}$$

Where ε_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:

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

Where ω_h is the relaxation angular frequency and β is the distribution coefficient of high frequency relaxation. The dielectric increment can be defined as:

$$\Delta\varepsilon_h = \frac{2}{9\pi^2}\frac{\varphi G_h^2\kappa}{\omega_h^{\ 2}\varepsilon_0^{\ 2}\varepsilon_S v} \quad \text{(S7)}$$

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

$$G_h = 2qM_i\rho_h(1-\frac{1}{2\pi\eta l_B M_i}) \quad \text{(S8)}$$

Whereη is the viscosity of the solvent, and the linear charged density of counterions that cause HF relaxation can be given as:

$$\rho_h = \frac{\pi\varepsilon_0\varepsilon_s\zeta^2}{4k_BT}(\frac{\kappa a K_1(\kappa a)}{K_0(\kappa a)})^2 - \frac{\pi\varepsilon_0\varepsilon_s\zeta^2(\kappa a)^2}{4k_BT} \quad \text{(S9)}$$

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