



Soft Matter

## Supplementary Information

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### Revisiting the colloidal fundamentals of water-dispersible polyesters: Interactions and self-assembly of polymer nanoaggregates in water

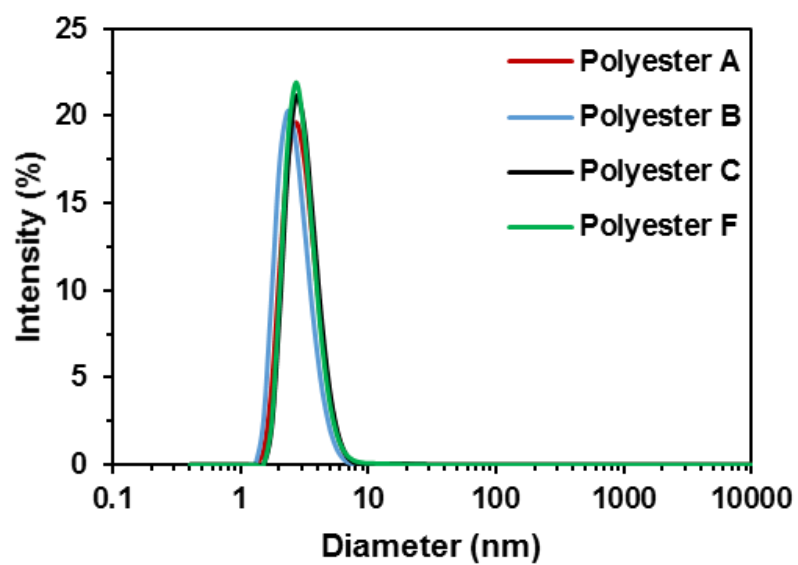
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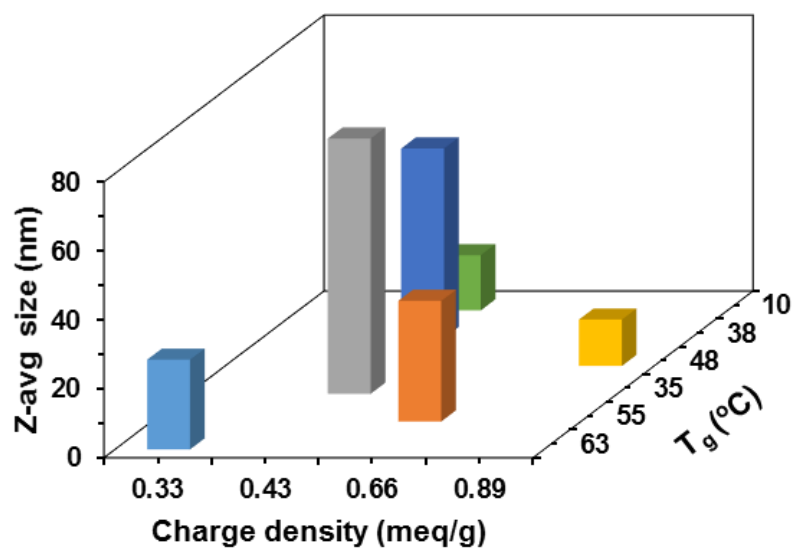
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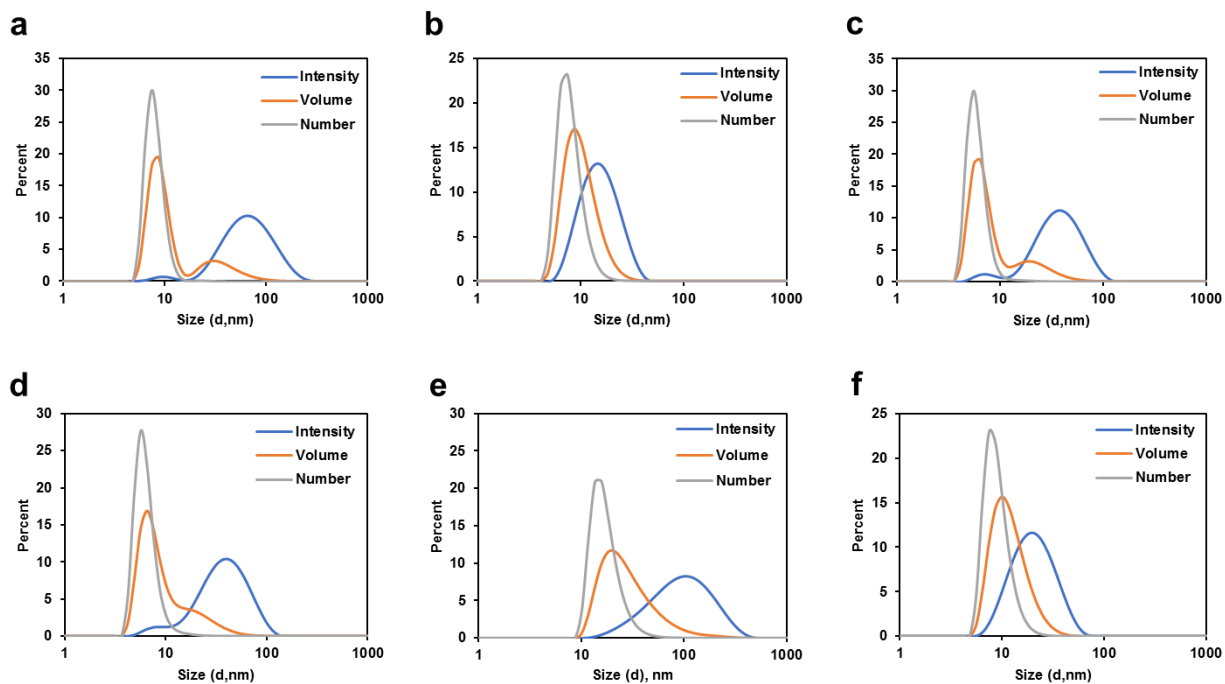


**Fig. S1** Intensity distributions based on volume from DLS experiment with 100 g/L polyesters in DMF.

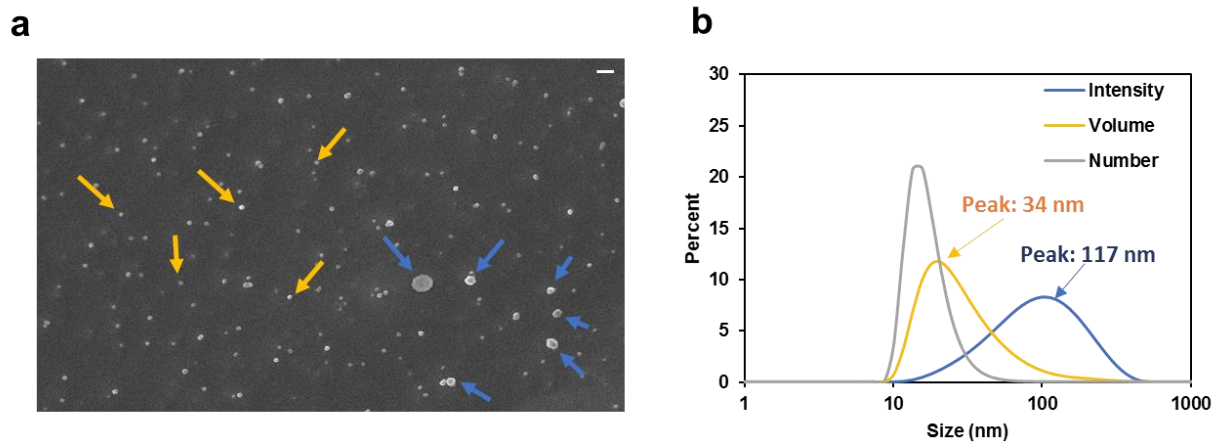


**Fig. S2** Effect of acid and glycol composition of the polyesters on the size of the polyester nanoparticles in water.

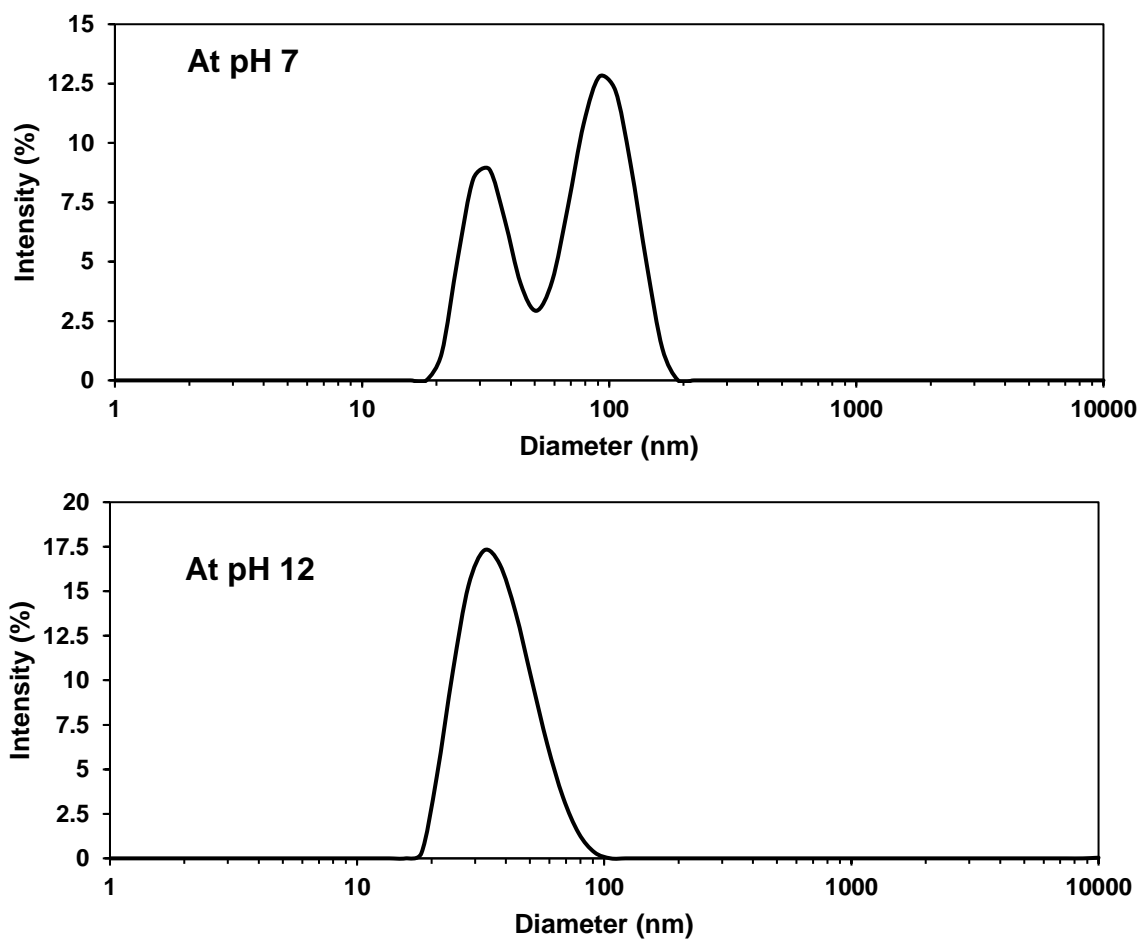
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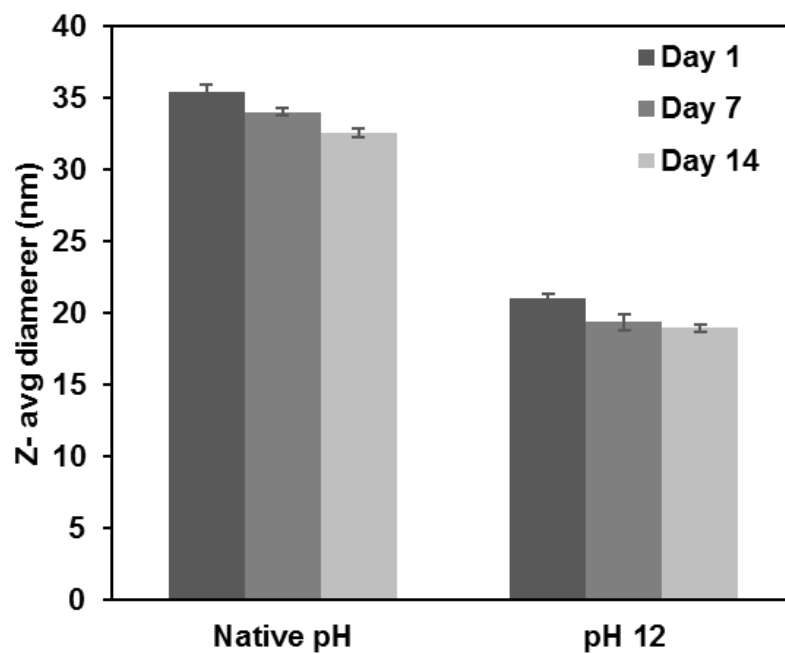
**Fig. S3** Size distribution analysis based on intensity, volume and number from DLS experiment with 0.1% suspension of (a) polyester A, (b) polyester B, (c) polyester C, (d) polyester D, (e) polyester F, and (f) polyester E in water showing the polydisperse nature of the samples.



**Fig. S4** Examples of the polydispersity of the polyester nanoparticles. (a) Cryo-SEM experiment and (b) DLS experiment with 1g/L polyester E. Scale bar = 100 nm.

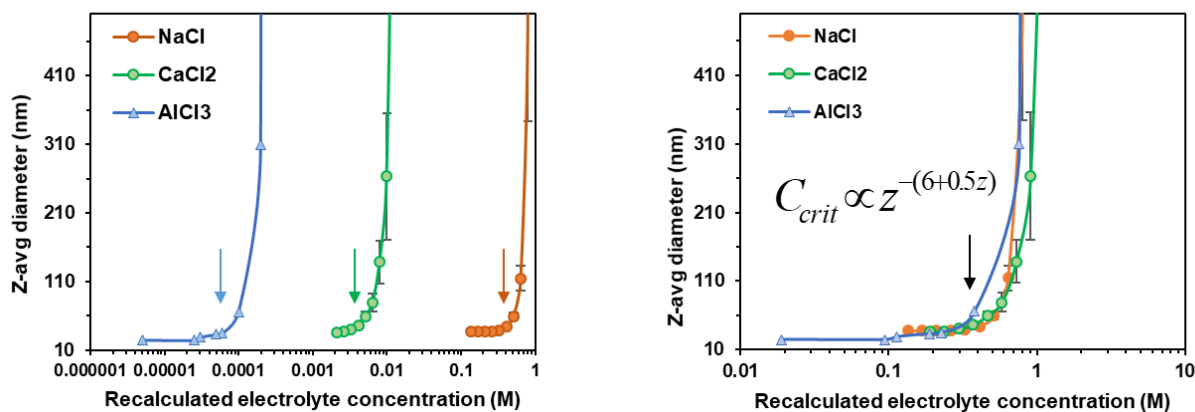


**Fig. S5** Effect of pH on the size distribution of polyester A nanoparticles. Multimodal analysis of intensity distributions from DLS experiment of 0.1% polyester A in water at pH 7 and 12 shows the bimodal distribution converts into monomodal at pH 12.



**Fig. S6** Long-term size measurement of polyester C in water at pH 7 and pH 12 showing that the change in particle size at high pH is not a result of alkaline hydrolysis.

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**Fig. S7** Validation of DLVO theory for polyester B by using multivalent electrolytes. (a) The Z-avg particle size of polyester B in water with different amounts of NaCl, CaCl<sub>2</sub>, and AlCl<sub>3</sub>. (b) Fitting experimental data by recalculating x-axis values for electrolytes according to the slightly modified Schulze-Hardy rule  $C_{crit} \propto z^{-(6+0.5z)}$ . The arrows indicate the  $C_{crit}$  values for different electrolytes.



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### Derivation of Schulze-Hardy rule from DLVO theory

The relationship of critical coagulation concentration ( $C_{crit}$ ) on the counterion valency ( $z$ ) for electrostatically stabilized colloidal system (i.e.,  $C_{crit} \propto z^{-6}$ ) is historically known as Schulze-Hardy rule. This empirical rule has been derived directly on the basis of the classic DLVO theory in many literature sources.<sup>1-4</sup> The derivation is attached herein.<sup>1</sup>

According to DLVO theory, two spherical particles interact in a liquid medium through the *van der Waals* (attractive) and electrostatic (repulsive) interactions. Thus the total interaction potential for the spherical particles interacting at constant potential can be described by following relationship.

$$W(D) = W_{electrostatic} + W_{vdW} \quad (1)$$

$$= (64\pi kTR\rho_{\infty}\gamma^2/\kappa^2) e^{-\kappa D} - AR/12D \quad (2)$$

Where  $D$  = distance between particle surfaces;  $k$  = Boltzmann constant;  $T$  = temperature (K);  $R$  = radius of particles;  $\rho_{\infty}$  = bulk concentration of ions;  $e$  = elementary charge;  $\kappa^{-1}$  = Debye length;  $A$  = Hamaker constant;  $\gamma = \tanh(ze\psi_s/4kT)$  where  $z$  = valency of counterion,  $\psi_s$  = surface potential

By definition, at the approximate moment of coagulation, the following relationships hold true.

$$W(D_{crit}) = 0 \quad (3)$$

$$(dW/Dd)_{crit} = 0 \quad (4)$$

Solving Eq. 2 with respect to Eq. 3 leads to

$$k^2/\rho_{\infty} = 768\pi kTD \gamma^2 e^{-\kappa D}/A \quad (5)$$

Solving Eq. 2 with respect to Eq. 4 leads to

$$\kappa D = 1 \quad (6)$$

Combination of Eq. 5 and 6 leads to

$$k^3/\rho_{\infty} = 768\pi kT \gamma^2 e^{-1}/A \quad (7)$$

Or,  $k^6/\rho_{\infty}^2 \propto (T \gamma^2/A)^2 \quad (8)$

Now since Debye length is defined by following equation

$$\kappa = (\sum \rho_{\infty} e^2 z^2 / \epsilon \epsilon_0 kT)^{0.5} \quad (9)$$

where  $\epsilon$  = permittivity of the medium;  $\epsilon_0$  = permittivity of vacuum;

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Or, 
$$k^6 / \rho^2_{\infty} \propto (T \gamma^2 / A)^2 \quad (10)$$

Combination of Eq. 10 and 8 leads to

$$z^6 / \rho_{\infty} \propto \varepsilon^3 T^5 \gamma^4 / A^2 \quad (11)$$

At high surface potential,  $\gamma = \tanh(ze\psi_s/4kT) = 1$

Therefore, Eq. 11 can be written as,

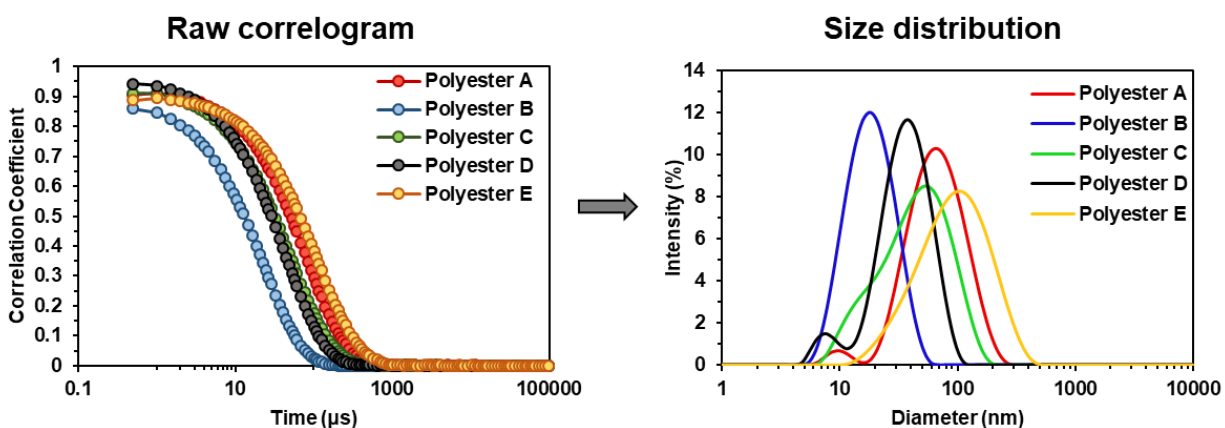
$$z^6 / \rho_{\infty} \propto \text{constant}$$

Or, 
$$\rho_{\infty} \propto z^{-6}$$

This way, the critical concentration of ions at the moment of coagulation ( $C_{crit}$ ) is inversely related to the sixth power of the counterion valency ( $z$ ), which is empirically known as Schulze-Hardy rule and can be directly derived from DLVO theory as described here.

### Processing of dynamic light scattering data<sup>5</sup>

The dynamic light scattering data were processed using the default software “Zetasizer” from Malvern Instruments. Using a digital correlator, the instrument correlates the intensity fluctuation over time by comparing the degree of similarity between two signals over a period of time in presence of noise (i.e., light scattering from solvent molecules) and constructs correlograms (Fig. S6). The software then analyzes the correlograms using cumulant analysis algorithm and distribution analysis algorithm.



**Fig. S6** Example of raw correlogram and resulted size distribution graph for processing DLS data.

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**Cumulant (or Z-average) analysis:** In this analysis method, a single particle size is assumed, and a single exponential fit is applied to the autocorrelation function and the sample is characterized by an intensity weighted mean hydrodynamic size (Z-average) and a polydispersity index (PDI). Cumulant analysis fits the correlogram into a single exponential relationship as shown below

$$G_2(\tau) = \langle I(t) \bullet I(t + \tau) \rangle = A[1 + B \exp(-2\Gamma \tau)]$$

Where A is the intercept,  $\Gamma$  is the correlation decay which is related to the overall mean size, and B is the baseline.

In order to account for the polydispersity of the Gaussian size distribution, the expression is extended to the following and then linearized-

$$G_2(\tau) = \langle I(t) \bullet I(t + \tau) \rangle = A[1 + B \exp(-2\Gamma \tau + \mu_2 \tau^2)]$$

$$y(\tau) = \frac{1}{2} \ln[G_2(\tau) - A] \cong \frac{1}{2} \ln AB - \langle \Gamma \rangle \tau + \frac{\mu_2}{2} \tau^2 = a_0 - a_1 \tau + a_2 \tau^2$$

Where the first moment  $a_1$  is equal to the  $\Gamma$  correlation decay rate which is directly related to diffusion coefficient and hydrodynamic radius by Stokes-Einstein equation and the second moment is related to the distribution width or the PDI according to following relationships.

$$\Gamma = a_1 = Dq^2; \quad PDI = \frac{2a_2}{a_1^2}$$

$$q = \frac{4\pi n}{\lambda_0} \sin\left(\frac{\theta}{2}\right); \quad R_H = \frac{kT}{6\pi\eta D}$$

Where  $q$  = scattering vector;  $n$  = refractive index of medium;  $\theta$  = scattering angle;  $\lambda_0$  = vacuum wavelength of the laser;  $R_H$  = hydrodynamic radius;  $D$  = translational diffusion coefficient;  $k_B$  = Boltzmann's constant;  $T$  = thermodynamic temperature;  $\eta$  = dynamic viscosity.

### References

1. J. N. Israelachvili, in *Intermolecular and Surface Forces (Third Edition)*, Academic Press, San Diego, 2011, ch. 14, pp. 291-340.
2. Z. Zhang, L. Zhao, Y. Li and M. Chu, *Mathematical Problems in Engineering*, 2015, **2015**, 5.
3. B. Derjaguin and L. Landau, *Acta Physicochim. USSR*, 1941, **14**, 633-662.
4. E. J. W. Verway and J. T. G. Overbeek, *Theory of the stability of lyophobic colloids*, Elsevier, Amsterdam, 1948.
5. Zetasizer documentation available via [www.malvern.com](http://www.malvern.com).