## Soft Matter



# Supplementary Information

# Mechanism and control of "coffee-ring erosion" phenomena in structurally colored ionomer films

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Polyester	%Acid moiety		%Glycol moiety		Molecular weight	
Sample No.	IPA	SSIPA	CHDM	DEG	Mn	$\mathbf{M}_{\mathbf{w}}$
1	82	18	25	75	4925	16921
2	91	9	46	54	10515	29382
3	82	18	75	25	9855	19742
4	73	27	46	54	10180	20552
5	82	18	46	54	10301	21358
6	82	18	46	54	12486	27510
7	82	18	46	54	7240	18200

Table S1: Composition of the sulfopolyesters

 Table S2: Composition of carboxylated polyester

Polyester	%Acid moiety	%Glycol moiety	%carboxylate moiety	Molecular weight	
Sample No.	CHDA <sup>1</sup>	TMCD <sup>2</sup>	DMPA <sup>3</sup>	$\mathbf{M}_{\mathbf{n}}$	$\mathbf{M}_{\mathbf{w}}$
9	100	100	20	2952	8248

<sup>1</sup>CHDA: 1,4-Cyclohexanedicarboxylic Acid <sup>2</sup>TMCD: 2,2,4,4-Tetramethyl-1,3-cyclobutanediol <sup>3</sup>DMPA: Dimethylolpropionic acid



**Fig. S1** The hydrodynamic diameter of the polyester nanoparticles from DLS experiment. The size of the nanoparticles varied with polyester composition whereas molecular weight had no effect on the nanoparticle size.



Fig. S2 AFM with sulfopolyesters nanofilm.

Film No.	Thickness of film t (nm)	Constructive interference wavelength calculated from Eqn 5 $\lambda$ (nm)				Predicted color for visible wavelengths when m =2	Actual structural colors on the films
		<b>m</b> = 1	<b>m</b> = 2	m = 3	<b>m</b> = 4		
#1	275	860	430	286	215	<mark>430 nm</mark>	
#2	325	1007	503	335	251	<mark>503 nm</mark>	a mar a co
#3	365	1132	565	377	283	<mark>565 nm</mark>	

 Table S3: Correlation of film thickness with structural color.



**Fig. S3** Profilometry thickness profile of pattern generated as a result of NaCl solution evaporation overlaid on polyester film shows the erosion phenomenon was suppressed in presence of electrolyte.



**Fig. S4** DLS with polyester nanoparticle before film formation (original dispersion) and after film redispersion in the damaging water droplet.



**Fig. S5** (a) Dried profile is a complex function of nanoparticle redispersion and water evaporation. (b) Sessile droplet drying of polyester dispersion can be used to understand the effect of evaporation first.



**Fig. S6 (a)** Coffee-ring formation for all concentrations, **(b)** thickness of the thin film inside of the deposited pattern as a function of polymer concentration. Structural color inside the film depends on a strict concentration range of the polymer dispersion.



Fig. S7 (a) Schematic of sessile polyester dispersion droplet from side-angle where  $\theta$  denotes the contact angle, *b* denotes the diameter of the contact area (baseline), *h* denotes the droplet height, (b) change in contact angle as a function of time during droplet evaporation showing constant contact area based evaporation, (c) contact angle of the dispersion droplet as a function of polymer concentration, (d) contact angle and the height of the dispersion droplet as a function of droplet volume.

### **Higher MW**



**Fig. S8 Effect of MW on the coffee-ring erosion.** MW had no effect on the coffee-ring erosion as all three polyester experienced similar water damage. Scale bar indicates 1 mm.

# Higher MW

**Fig. S9 Effect of MW on the coffee-ring erosion of the heat-treated films.** The water resistance was improved to the same extent for the varying MW of the polyesters. Scale bar indicates 1 mm.



**Fig. S10. Coffee-ring erosion vs. classical coffee-ring phenomenon. Coffee-ring erosion:** Postdeposition water damage on polyester film is a complex function of nanoparticle redispersion and water evaporation. **Classical coffee-ring:** Sessile droplet drying of polyester dispersion creates similar deposition profile as coffee-ring erosion and therefore sessile droplet drying can be used to understand the drying nature of the polyester nanoparticles.