Supporting Information

Explanations for Water Whitening in Secondary Dispersion and Emulsion Polymer Films

Yang Liu, [1] *Agata Gajewicz,*[1,] *Victor Rodin,*[2,] *Willem-Jan Soer,*[3] *Jürgen Scheerder,*[3] *Guru Satgurunathan,*[3] *Peter J. McDonald*[1] *and Joseph L. Keddie*[1]

[1]Department of Physics, University of Surrey, GU2 7XH, Guildford, UK

[2]Institute of Organic Chemistry, Johannes Kepler University, Linz, Austria

[3]DSM Coating Resins B.V. Sluisweg 12, 5145 PE Waalwijk, The Netherlands

Correspondence to: Joseph L. Keddie (E-mail: j.keddie@surrey.ac.uk)

Secondary Dispersion Process

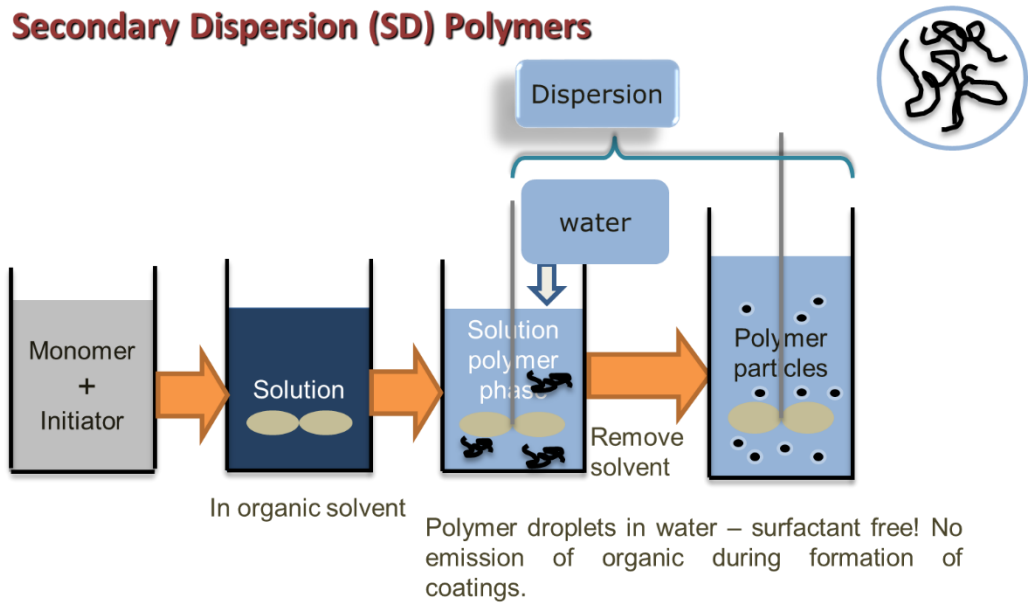

Figure S1. Schematic representation of the stages in the preparation of secondary dispersions of polymers. After solution polymerization in an organic solvent, the polymer is neutralized with N,N-dimethyl ethanolamine (DMAE) and dispersed in water. The solvent is removed under vacuum to leave a dispersion of polymer in water.

Table S1. Characteristics of Three Main Forms of the Copolymer

Polymer type	Surfactant present?	Particle Size (nm)	Particle Size Dispersity	Molecular weight, M_w (kDa)	Polydispersity Index, M_w/M_n	T_g (°C)
Em	Yes	98	0.25	55	4.6	29
SD	No	200	0.24	32	5.3	33
SL	No	-	-	32	5.3	35

Solid Echo Analysis

Table S2 and Table S3 summarize the intensities of mobile ^1H components and their increments in percentage for the different polymers after immersion in H_2O and D_2O for 4 hours and 24 hours. Data for SL and Em-MEK after soaking for 168 hours are also included. It can be seen that the SL films sorb the least amount of water compared to the others, followed by the Em films cast from MEK. Em-MEK films sorb a significantly less amount of water because of the absence of boundaries between particles. Compared to the SL film, the presence of surfactant leads to more sorption of liquid water. After 168 hours soaking, the intensities of mobile ^1H components of Em-MEK reach a level that is approximately four times greater than in the SL film. It is surprising to find that the DEm films sorbs more water than the Em films before being dialyzed, as usually water sorption is correlated positively with the amount of hydrophilic species. The small molecules in the water phase (*e.g.* surfactants and water-soluble oligomers) are expected to contribute to the water sorption in the final film. When they are removed by dialysis, one might expect the water sorption to fall. The experimental result may be explained by the loss of surfactant that de-stabilizes the particles. It could make it easier for water to reach the hydrophilic regions, clustering more readily. The SD films take up less water than the Em films after removal of surfactant by dialysis. This is expected when there is a lower concentration of hydrophilic species. The dialysis procedure cannot remove all of the hydrophilic components, and so the dialyzed Em films never reach the results for the SD films.

Table S2. Intensities % of Mobile ^1H Components for Various Dry Polymers

Soaking Medium*	Em	DEm	Em-MEK	SD	SD-pre	SL
H_2O	5.4	3.3	10.7	7.5	10.7	7.3
D_2O	5.9	3.2	10.9	7.5	10.5	7.6

*Polymers were soaked in H_2O or D_2O after these measurements in the dry state.

Table S3. Differences in Intensity % of Mobile ^{1}H Components for Various Polymers after Immersing in H_2O and D_2O in Comparison with the Corresponding Dry Materials

Soaking time (h)	Medium	Em	DEm	Em-MEK	SD	SD-pre	SL
4	H_2O	4.4	6.4	3.1	3.6	5.6	0.2
4	D_2O	0.4	1.1	0.7	0.5	0.8	0.2
24	H_2O	10.8	21.0	7.2	9.4	14.6	0.8
24	D_2O	1.8	1.6	2.4	1.4	3.4	0.3
168	H_2O			11.7			2.8
168	D_2O			4.8			1.2

Table S4. Calculations of the Average Radius of Water Regions Inside Em, SD and DEm Films

Polymer	Water Immersion Time (h)	Correlation Coefficient R^2	C ($\times 10^9$ nm^4)	ϕ_w	R (nm)
Em	4	0.938	2.39	0.04	6.2
	8	0.993	6.12	0.06	7.6
	16	0.997	10.80	0.08	8.4
	24	0.998	14.40	0.09	9.3
	120	0.995	28.80	0.15	10.2
	144	0.997	44.90	0.17	12.3
SD	24	0.854	0.70	0.08	3.6
	120	0.960	1.78	0.11	4.7
DEm	4	0.997	2.89	0.06	6.2
	24	0.999	10.90	0.19	6.4
	120	0.999	14.94	0.27	6.5