Electronic Supplementary Material (ESI) for Soft Matter

Supporting Information

Charged microcapsules for controlled release of hydrophobic actives I:

Part I: Synthesis and characterization

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Microencapsulation

As mentioned in the article, the microencapsulation using only PDADMAC without any TC4 in the oil phase did not result in microcapsule. Instead a solid PMMA *macrocapsule* was formed. Yet, the oil was clearly inside the macrosphere since no phase separated oil layer was visible on top of the water surface

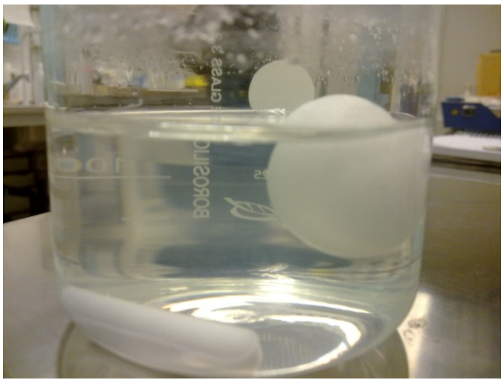

Figure S1. Result of microencapsulation using PDADMAC in the water phase.

Light microscopy

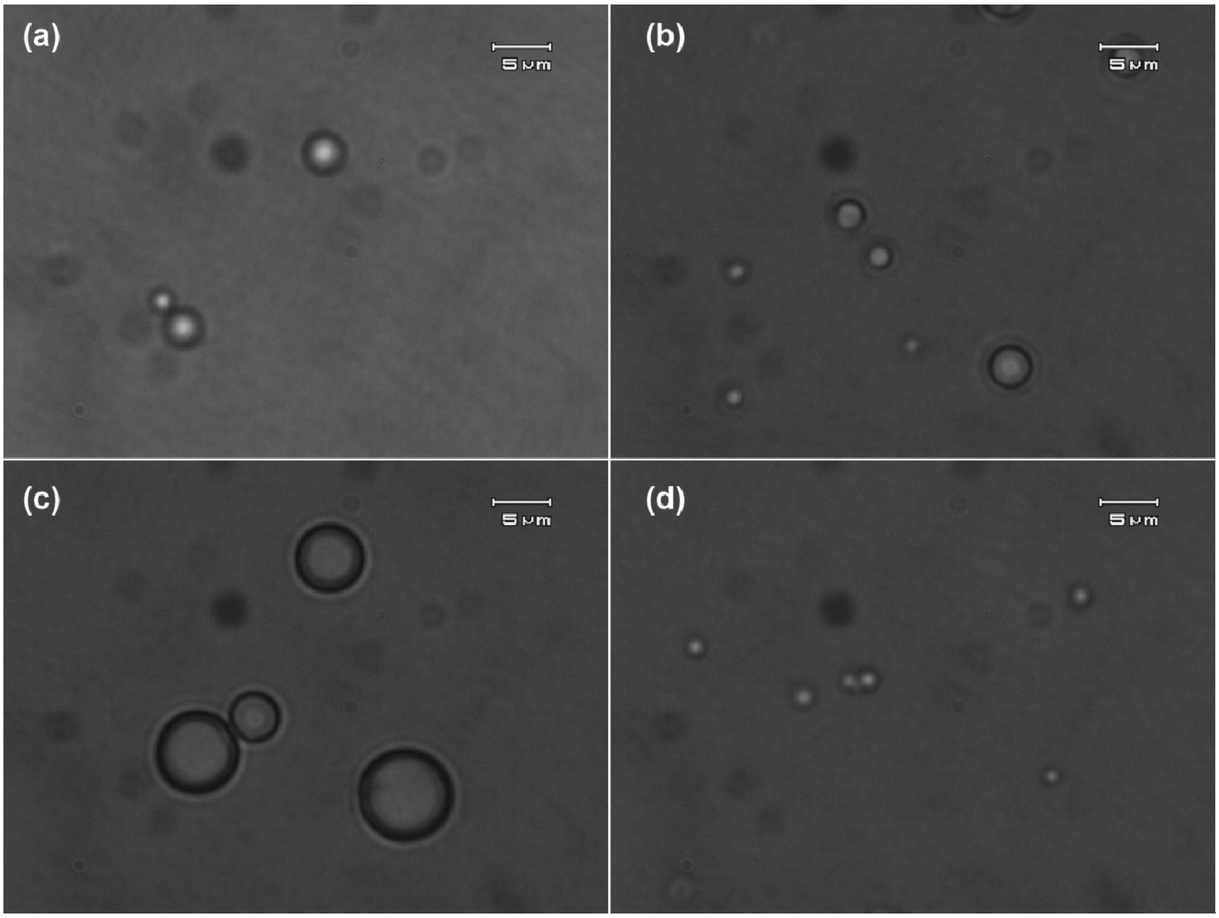

Figure S2. Light microscope photos of microcapsules prepared with different dispersants; a) PMAA, b) 600)-*b*-4600, c). 4000-*b*-9300 and d) 4300-*b*-17500.

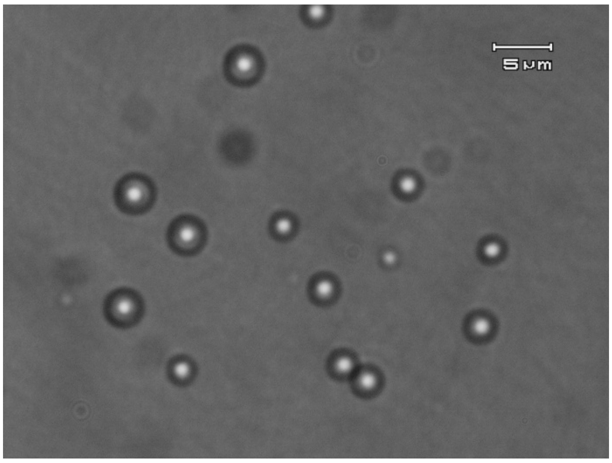

Figure S3. Light microscope photos of microcapsules prepared with PDADMAC-TC4.

Optical tensiometry

Table S1. Summary of the data obtained from pendant drop and contact angle measurements. Index w, s, o indicate water, solid (PMMA or PMMA+TC4) and oil (dodecane or dodecane+TC4) respectively. Contact angles ϕ are given in degrees ° and surface/interfacial tensions are given in mN/m.

	air	o in w	DIM				s in o	
				s in w				
	γ	γ(o-w)	γ(DIM-w)	ϕ(w)	γ(s-w)	s-DIM	ϕ(w)	γ(s-o)
Pure w	72.8	52.5	48.5	73.8		4.00	100	8.5[b]
600-*b*-4600	60.5	37.3	35.5	95.7	0.44			
4000-*b*-9300	69	45.3	40.1	88.3	1.19			
4300-*b*-17500	72	42.8	40.7	88.9	0.78			
5500-*b*-6200	72	41.4	41.1	83.2	4.87			
PDADMAC	73	51.7						
TC4 in o[a]	25	2.57					89	18.4
TC4 in s[a]				108	-3.65	8.30		

[a] The aqueous phase contain PDADMAC. [b] Using γ(s-w)=17.5 mN/m as obtained from contact angle measurements of water on PMMA, see Table S3

Dynamic surface tension

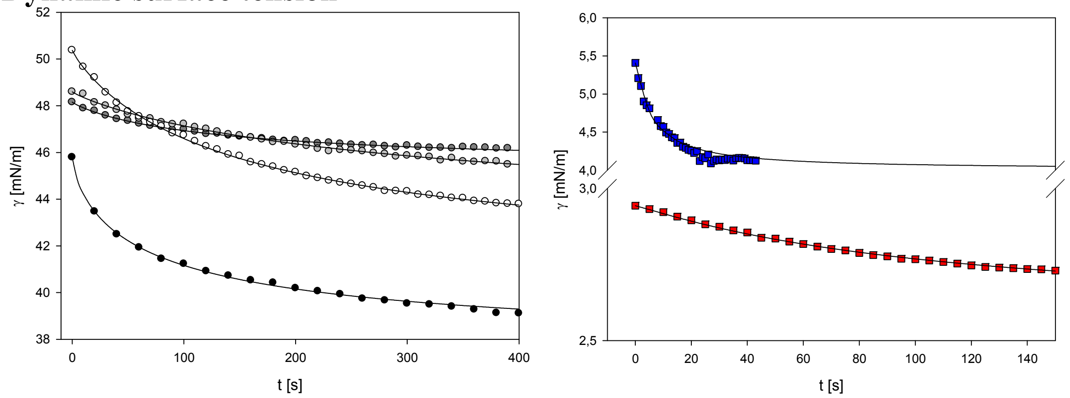

Figure S4. Oil-water interfacial tension decay for the different dispersant systems. Left; 600-b-4600 (●), 4000-b-9300 (●, dark grey), 4300-b-17500 (●,grey) 5500-6200 (○, white). Right; w(PDADMAC)-o(TC4) (■, red) and w-o(TC4) (■, blue).

The fits of the kinetic surface tension were generally very good (R^2>0.995). When comparing the different block copolymers, the obtained characteristic relaxation time τ follows more or less the size of the copolymer. The dimensionless parameter n is slightly smaller for 600-*b*-4600 (the smallest and most hydrophilic block copolymer) which obeys the notion that more hydrophobic surfactants obtain higher values of n. The non-polymeric surfactant TC4 has the smallest characteristic relaxation time which is logical given its relatively small size. The interfacial tension decay is much slower for the PDADMAC-TC4 system although with a very similar value of n. The slow kinetics is most likely due to the slow continuous adsorption of PDMADMAC to the interface.

Table S2. Parameters from adsorption isotherms obtained with QCM-D and pendant drop measurements.

Emulsifier	QCM-D		Interfacial tension		
	$\Gamma_{\max}$ [ng/cm^2]	K [wt%$^{-1}$]	γ_e [mN/m]	τ [s]	n
PMAA	402.0	33.78			
600-*b*-4600	266.1	6039	37.3	77.98	0.721
4000-*b*-9300	405,9	454.5	45,3	138.5	0.906
4300-*b*-17500	302.9	4371	42,8	339.3	0.894
5500-*b*-6200	496.9	253.2	40,8	161.4	0.893
PDADMAC-TC4	3056	3810	2.57	110.5	1.074
w-TC4			4.01	5.948	1.087
PDADMAC-o/PMMA	82.79	3815	51.7	4.526[a]	2.407[a]

[a] The fitted dynamic interfacial values should be taken with caution. The noise of the data was very large and the fitted parameters exhibited large standard deviations.

Surface free energy calculations

The surface free energy calculations for the TC4 functionalized surface are presented in Table S3 and Table S4. The basic character is increased as compared with pure PMMA which is reasonable since TC4 is an anionic surfactant. The small acidic contribution is most likely due to the presence of Na^+ counter ions. Furthermore, the van Oss results are very similar to the corresponding Fowkes results.

Table S3. Liquids used for surface energy calculation and their respective surface tension and surface tension components. $\boldsymbol{\phi_c}$ indicate the contact angle in air between the liquid and the TC4 functionalized PMMA surface.

Liquid	γ^{TOT}	γ^{LF}	γ^{AB}	γ^{+}	γ^{-}	ϕ_c	
						PMMA+TC4	PMMA
Water	72.8	21.8	51.0	25.5	25.5	42.3	71.8
Glycerol	64.0	34.0	30.0	3.92	57.2	24.5	
Diiodomethane	50.8	50.8	0	0	0	41.5	40.3
Formamide	58.0	39.0	19.0	2.28	39.6	17.1	57.1

Table S4. Obtained surface energy and surface energy parameters for the TC4 functionalized PMMA surface. In addition to the van Oss acid-base results, calculations using the Fowkes formalism are also presented.

van Oss			Fowkes		
	PMMA+TC4	PMMA		PMMA+TC4	PMMA
γ^{TOT}	57.4	39.5	γ^{TOT}	58.7	42.2
γ^{LF}	38.5	39.5	γ^{d}	37.3	35.4
γ^{AB}	18.9	0	γ^{p}	21.4	6.85
γ^{+}	1.38	0			
γ^{-}	6.85	3.65			
error	0.41				

QCM-D

All polymers adsorbed more or less according to a Langmuir isotherm. The block copolymer 5500-*b*-6200 displayed the largest deviation with an almost linear increment when the concentration was presented on a logarithmic scale. It is important to keep in mind that free polymers are the most plausible adsorbents. Clearly, a significant amount of 5500-*b*-6200 was aggregated as indicated by the opacity of the solution. At thermodynamical equilibrium, the adsorbed polymer is in equilibrium with both free polymer and aggregated polymer in the bulk.

During the QCM-D measurements, the system is not necessarily in equilibrium due to the slow kinetics of the polymers in the glassy aggregates. Therefore, the total concentration of block copolymer is most likely not equal to the concentration available for adsorption. This effect holds for all the block copolymers and is most significant for 5500-*b*-6200 which is the least water soluble one.

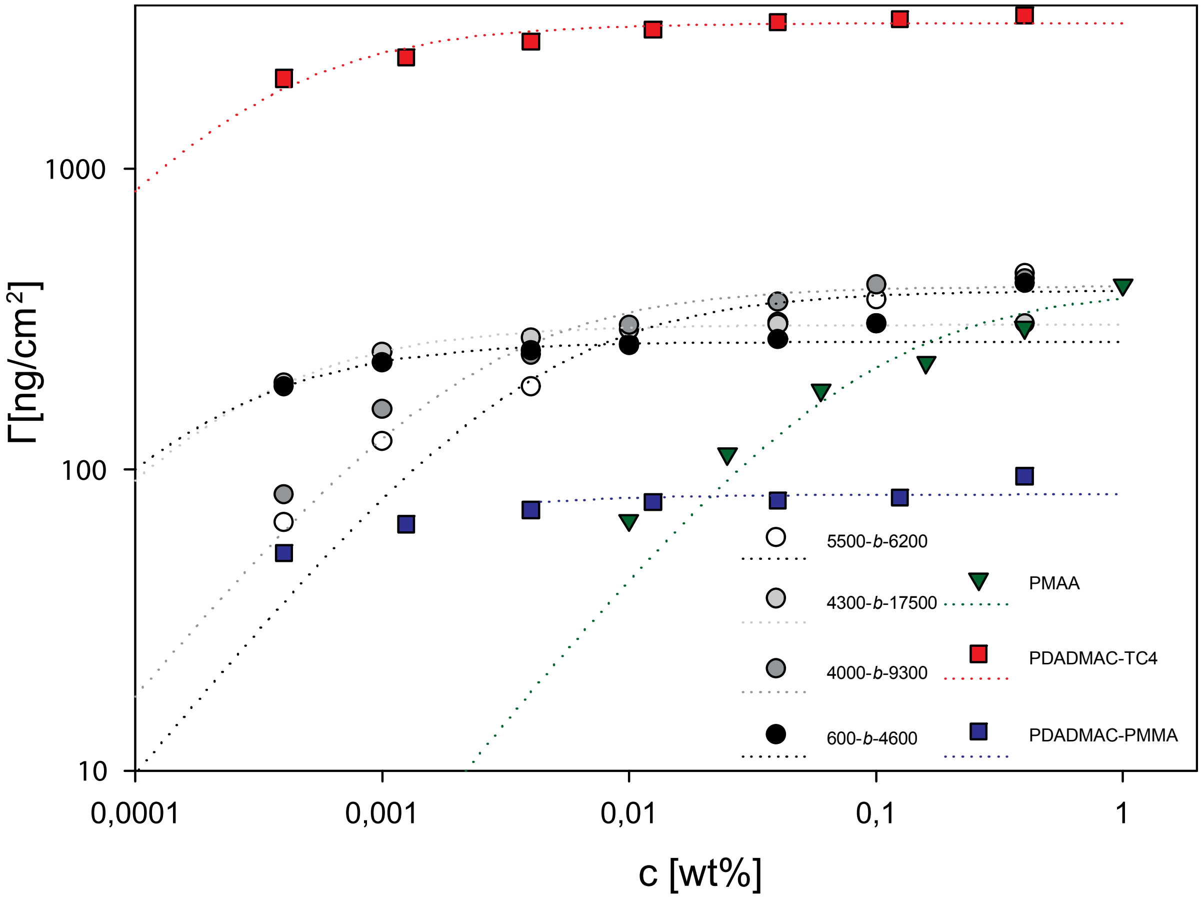

Figure S5. Adsorption isotherms on a log-log scale of 600-b-4600 (●), 4000-b-9300 (●, dark grey), 4300-b-17500 (●,grey) 5500-6200 (○, white), PMAA (▼, green), PDADMAC on a TC4 modified PMMA surface (■, red) and PDADMAC on a pure PMMA surface (■, blue) as measured with QCM-D.