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## Electronic Supplementary Information for:

### Co-Axial Capillaries Microfluidic Device for Synthesizing Size- and Morphology-Controlled Polymer Core-Polymer Shell Particles

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#### Operating conditions:

Fig. 2: Top,  $Q_I = 0.0012 \text{ mL}\cdot\text{min}^{-1}$ ;  $Q_M = 0.005 \text{ mL}\cdot\text{min}^{-1}$ ;  $Q_O = 0.06 \text{ mL}\cdot\text{min}^{-1}$ . Bottom,  $Q_I = 0.0035 \text{ mL}\cdot\text{min}^{-1}$ ;  $Q_M = 0.004 \text{ mL}\cdot\text{min}^{-1}$ ;  $Q_O = 0.05 \text{ mL}\cdot\text{min}^{-1}$ . Prepared in system I.

Fig. 3: (a)  $Q_O = 0.07 \text{ mL}\cdot\text{min}^{-1}$  and  $Q_M = 0.005 \text{ mL}\cdot\text{min}^{-1}$  in microfluidic system I;  $Q_O = 0.06 \text{ mL}\cdot\text{min}^{-1}$  and  $Q_M = 0.005 \text{ mL}\cdot\text{min}^{-1}$  in microfluidic system II;  $\mu_O = 1500 \text{ cP}$ ; (b)  $Q_O = 0.07 \text{ mL}\cdot\text{min}^{-1}$  and  $Q_I = 0.0012 \text{ mL}\cdot\text{min}^{-1}$  in microfluidic system I;  $Q_O = 0.06 \text{ mL}\cdot\text{min}^{-1}$  and  $Q_I = 0.0032 \text{ mL}\cdot\text{min}^{-1}$  in microfluidic system II;  $\mu_O = 1500 \text{ cP}$ ; (c)  $Q_M = 0.005 \text{ mL}\cdot\text{min}^{-1}$  and  $Q_I = 0.0012 \text{ mL}\cdot\text{min}^{-1}$  in microfluidic system I;  $Q_M = 0.005 \text{ mL}\cdot\text{min}^{-1}$  and  $Q_I = 0.0032 \text{ mL}\cdot\text{min}^{-1}$  in microfluidic system II;  $\mu_O = 1500 \text{ cP}$ ; (d)  $Q_O = 0.07 \text{ mL}\cdot\text{min}^{-1}$ ,  $Q_M = 0.005 \text{ mL}\cdot\text{min}^{-1}$  and  $Q_I = 0.0012 \text{ mL}\cdot\text{min}^{-1}$  in microfluidic system I;  $Q_O = 0.06 \text{ mL}\cdot\text{min}^{-1}$ ,  $Q_M = 0.005 \text{ mL}\cdot\text{min}^{-1}$  and  $Q_I = 0.0032 \text{ mL}\cdot\text{min}^{-1}$  in microfluidic system II;  $\mu_O = 1500 \text{ cP}$ .

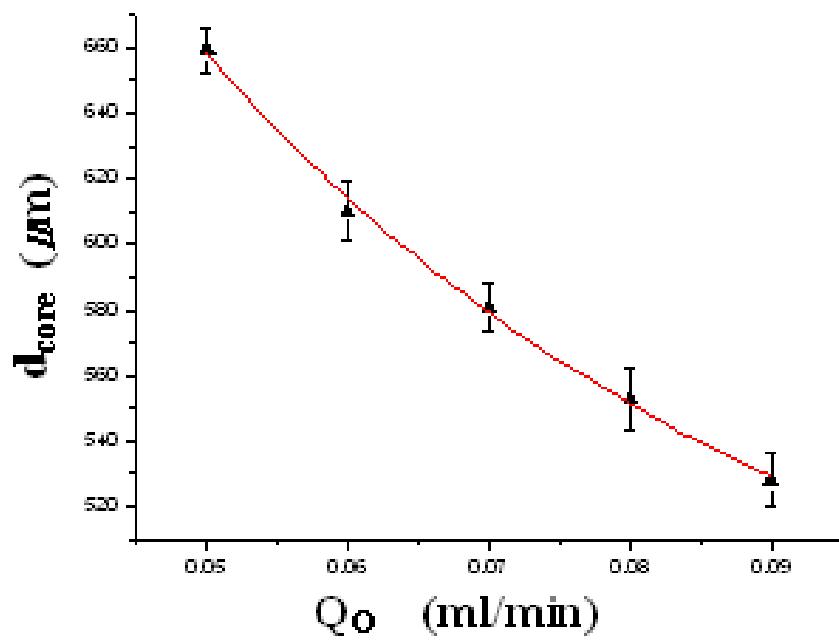
Fig. 5:  $\mu_O = 1500 \text{ cP}$ ,  $Q_O = 0.07 \text{ mL}\cdot\text{min}^{-1}$ ;  $Q_M = 0.006 \text{ mL}\cdot\text{min}^{-1}$ ;  $Q_I = 0.004 \text{ mL}\cdot\text{min}^{-1}$ (a,a');  $Q_I = 0.0006 \text{ mL}\cdot\text{min}^{-1}$ (b,b');  $Q_I = 0.0008 \text{ mL}\cdot\text{min}^{-1}$ (c,c') in microfluidic system I,  $\Delta = -650 \mu\text{m}$ .

**Table ESI.1** Sizes of the capillaries and experimental materials

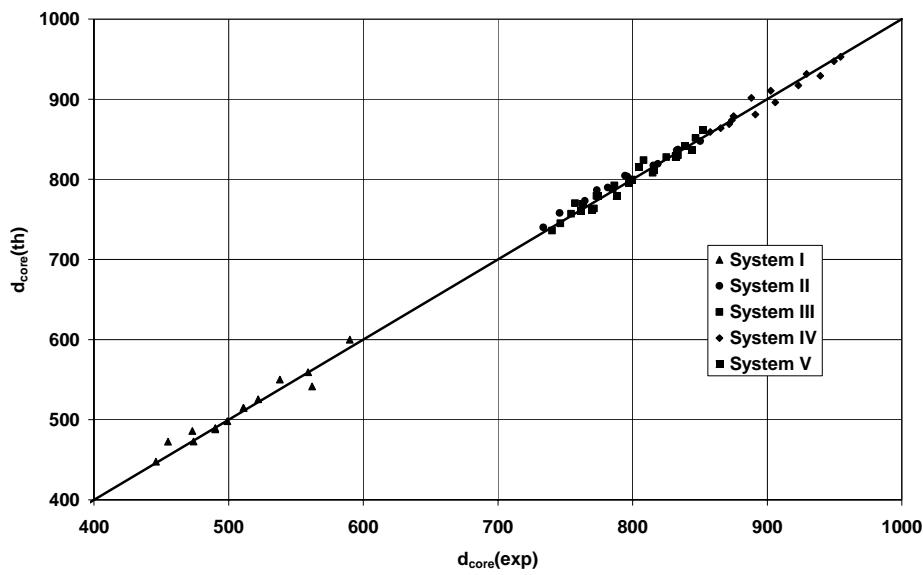
		System I			System II			System III			System IV			System V			System VI		
Capillary size		Inner diameter	Outer diameter	Material	Inner diameter	Outer diameter	Material	Inner diameter	Outer diameter	Material									
	Inner capillary	20 µm	90 µm	Glass	75 µm	360 µm	PEEK	100 µm	165 µm	Glass	150 µm	360 µm	PEEK	100 µm	360 µm	PEEK	100 µm	165 µm	Glass
	Middle capillary	150 µm	360 µm	PEEK	700 µm	850 µm	Glass	300 µm	760 µm	PTFE	700 µm	850 µm	Glass	530 µm	670 µm	Glass	250 µm	360 µm	Glass
	Outlet tubing	1600 µm	3200 µm	PTFE	1600 µm	3200 µm	PTFE	1600 µm	3200 µm	PTFE									
Inner fluid phase	acrylamide, 10 wt %; NN <sup>+</sup> -methylene-bisacrylamide, 1.5 wt %; Ammonium persulfate, 0.15 wt %;			acrylamide, 10 wt %; NN <sup>+</sup> -methylene-bisacrylamide, 1.5 wt %; Ammonium persulfate, 0.15 wt %;			acrylamide, 10 wt %; NN <sup>+</sup> -methylene-bisacrylamide, 1.5 wt %; Ammonium persulfate, 0.15 wt %;			acrylamide, 10 wt %; NN <sup>+</sup> -methylene-bisacrylamide, 1.5 wt %; Ammonium persulfate, 0.15 wt %;			acrylamide, 10 wt %; NN <sup>+</sup> -methylene-bisacrylamide, 1.5 wt %; Ammonium persulfate, 0.15 wt %;			distilled water			
	viscosity: 1.45 cP			viscosity: 1.45 cP			viscosity: 1.45 cP			viscosity: 1.45 cP			viscosity: 1.45 cP			viscosity: 0.98 cP			
Middle fluid phase	tripropylenglykol-diacylate, 93 wt %; Span80, 3.5% 1-hydroxycyclohexyl phenyl ketone,			tripropylenglykol-diacylate, 93 wt %; Span80, 3.5% 1-hydroxycyclohexyl phenyl ketone,			tripropylenglykol-diacylate, 93 wt %; Span80, 3.5% 1-hydroxycyclohexyl phenyl ketone,			tripropylenglykol-diacylate, 93 wt %; Span80, 3.5% 1-hydroxycyclohexyl phenyl ketone,			tripropylenglykol-diacylate, 93 wt %; Span80, 3.5% 1-hydroxycyclohexyl phenyl ketone,			tripropylenglykol-diacylate, 93 wt %; Span80, 3.5% 1-hydroxycyclohexyl phenyl ketone,			
	viscosity: 14.2 cP			viscosity: 14.2 cP			viscosity: 14.2 cP			viscosity: 14.2 cP			viscosity: 14.2 cP			viscosity: 14.2 cP			
Outer fluid phase	aqueous solution of methyl cellulose			aqueous solution of methyl cellulose															
	No.	viscosity (cP)		No.	viscosity (cP)		No.	viscosity (cP)		No.	viscosity (cP)		No.	viscosity (cP)		No.	viscosity (cP)		
	1	500		1	500		1	1300		1	1300		1	1300		1	1300		
	2	800		2	800		-	-		-	-		-	-		-	-		
	3	1100		3	1100		-	-		-	-		-	-		-	-		
	4	1400		4	1400		-	-		-	-		-	-		-	-		
	5	1600		5	1600		-	-		-	-		-	-		-	-		
	6	2000		6	2000		-	-		-	-		-	-		-	-		

**Table ESI 2.** Maximum standard errors ( $SE_{\max}$ , given in  $\mu\text{m}$ ) of experimental data plotted in Figure 3

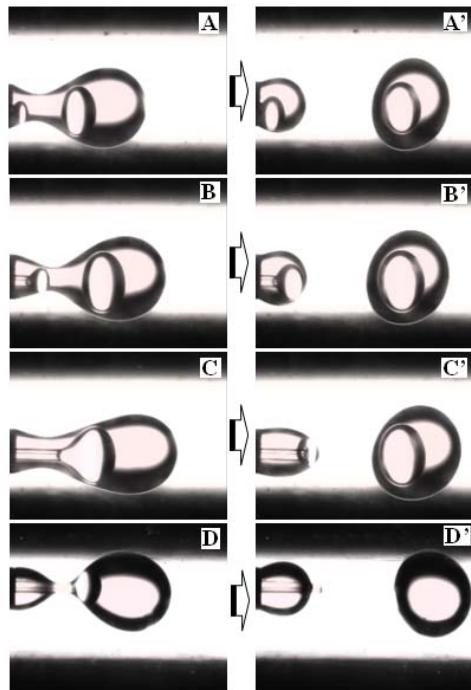
Graph	Data symbol					
	●	○	★	▲	Δ	■
3a	12.65	9.09	12.87	8.33	7.14	8.69
3b	11.77	10.52	11.08	5.45	9.36	9.33
3c	13.21	9.74	10.39	10.02	7.77	9.91
3d	10.63	13.92	11.6	7.38	6.64	6.37



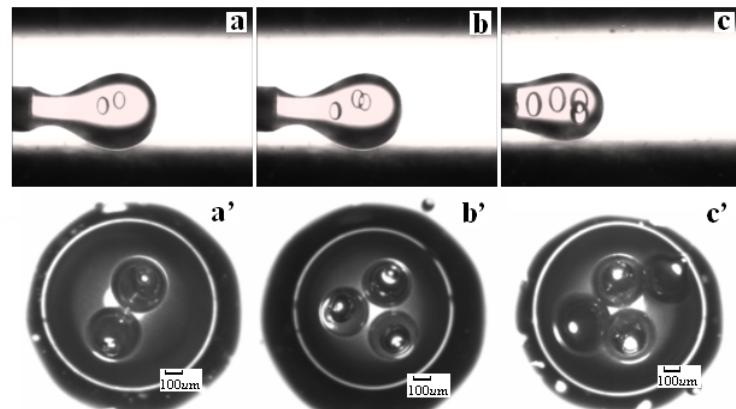
**Fig. ESI.1** Variation of the core droplet diameter with respect to the outer fluid flow rate at constant  $Q_O/Q_M$ .



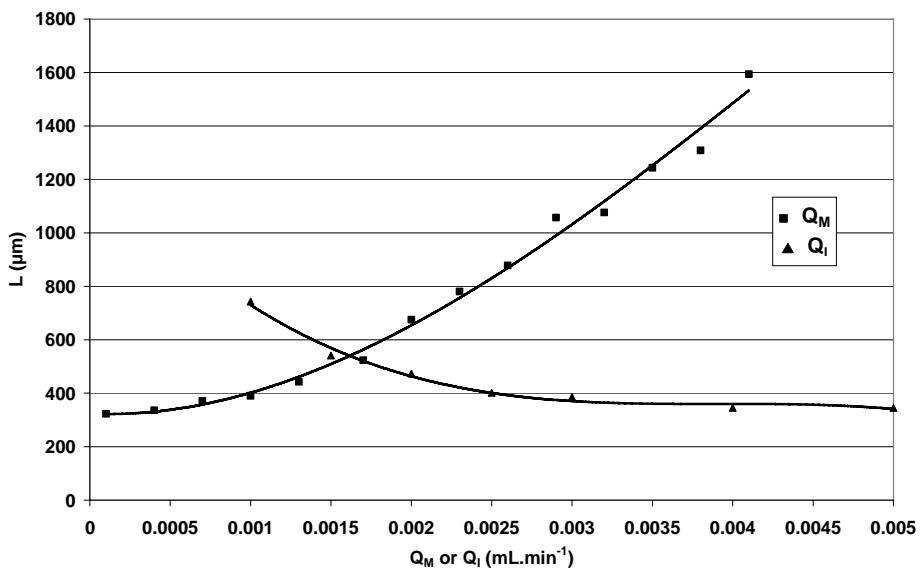
**Fig. ESI.2** Comparison between theoretical (th) and experimental (exp) core droplet diameter for the 5 systems tested. Solid line represents the first bisector.



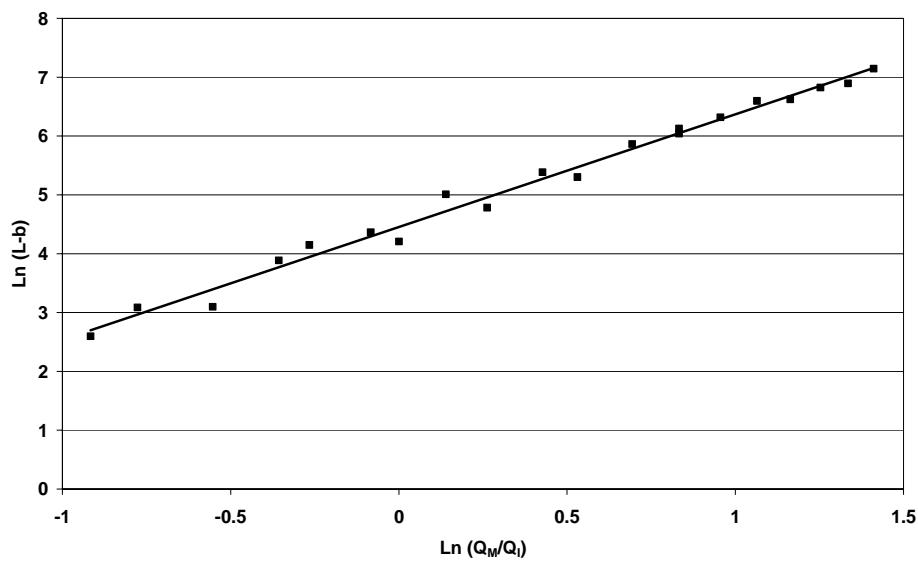
**Fig. ESL.3** Snapshots of the formation of core-shell droplets for different positive capillaries' tips relative position,  $\Delta=0$  (A,A');  $\Delta=146 \mu\text{m}$  (B,B');  $\Delta=360 \mu\text{m}$  (C,C');  $\Delta=480 \mu\text{m}$  (D,D'). Experimental conditions:  $Q_O = 0.07 \text{ mL}\cdot\text{min}^{-1}$ ;  $Q_M = 0.006 \text{ mL}\cdot\text{min}^{-1}$ ;  $Q_I = 0.0012 \text{ mL}\cdot\text{min}^{-1}$  in microfluidic system I,  $\mu_O = 1500 \text{ cP}$ .



**Fig. ESI.4** Optical microscopy images of the multiple core droplet formation in a co-axial capillaries microfluidic device with a negative capillaries' tips relative position (top) and the multiple poly(acrylamide) core-poly(propylene glycol-diacylate) shell particles obtained (bottom), core being labeled with an aqueous dye (Nigrosin, Aldrich). Experimental conditions:  $\mu_0 = 1500 \text{ cP}$ ,  $Q_0 = 0.07 \text{ mL} \cdot \text{min}^{-1}$ ;  $Q_M = 0.006 \text{ mL} \cdot \text{min}^{-1}$ ;  $Q_I = 0.004 \text{ mL} \cdot \text{min}^{-1}$ (a,a');  $Q_I = 0.0006 \text{ mL} \cdot \text{min}^{-1}$ (b,b');  $Q_I = 0.0008 \text{ mL} \cdot \text{min}^{-1}$ (c,c') in microfluidic system I,  $\Delta = -650 \mu\text{m}$ .



**Fig. ESI.5** Effects of the inner and middle fluid flow rates on the length of rod-like polymer particles obtained with microfluidic system VI ( $Q_I = 0.0023 \text{ mL}\cdot\text{min}^{-1}$  when  $Q_M$  is varying from  $0.0001 \text{ mL}\cdot\text{min}^{-1}$  to  $0.006 \text{ mL}\cdot\text{min}^{-1}$ ;  $Q_M = 0.0045 \text{ mL}\cdot\text{min}^{-1}$  when  $Q_I$  is varying from  $0.0025 \text{ mL}\cdot\text{min}^{-1}$  to  $0.014 \text{ mL}\cdot\text{min}^{-1}$ ;  $Q_o = 0.05 \text{ mL}\cdot\text{min}^{-1}$ ).



**Fig. ESI.6** Variations of the length of rod-like polymer particles with respect to the ratio between the middle and inner fluid flow rates. Solid line is derived from equation 4.