Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Complex Emulsions for Shape Control Based on Mass Transfer and Phase Separation

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Supporting Video Instructions

Video VS1 shows the changes in droplets that just exiting the microfluidic device.

Video VS2 shows the change process of droplets within 5 min.

Section 1. The phase diagram of PEGDA and DEX

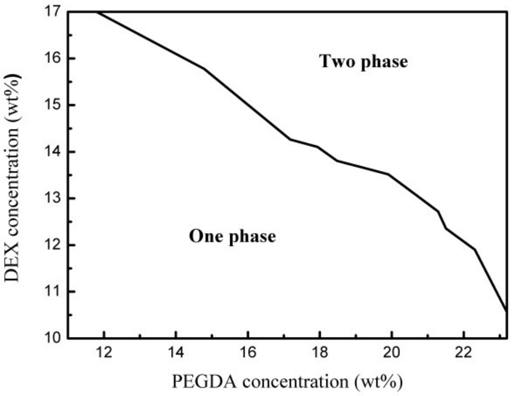

Figure S1. The phase diagram of PEGDA (Mn = 575) and DEX (Mw = 70000) at 20 °C.

Section 2. The ATPS droplets composed of PEGDA and DEX

In the preparation of ATPS droplets, DEX aqueous solution (10 wt% and 20 wt%) was used as dispersion phase I, with PEGDA aqueous solution (30 wt% to 75 wt%) as dispersion phase II, and liquid paraffin containing 2 wt% EM 90 as continuous phase. The flow rate of the dispersed phase was 75 μL/h with 4 mL/h for continuous phase.

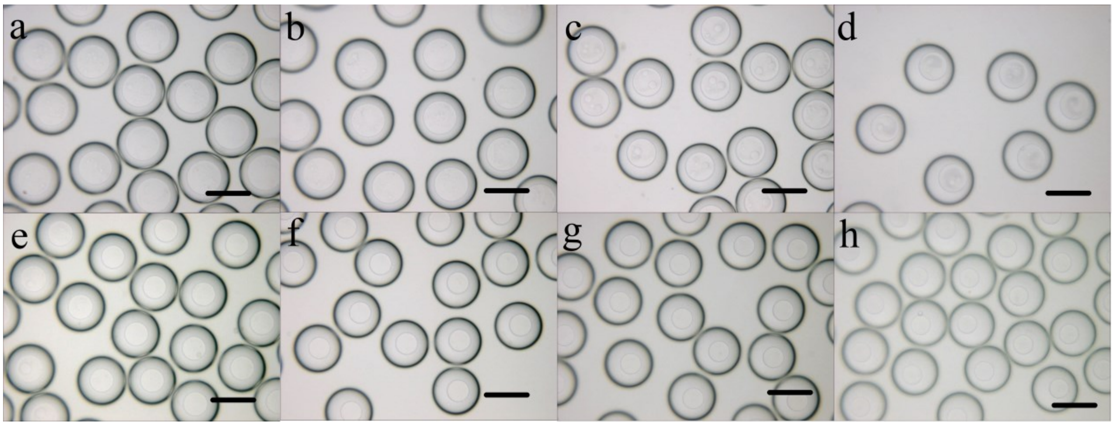

Figure S2. Optical microscopic images of ATPS droplets composed of PEGDA and DEX. The mass fraction ratios of PEGDA to DEX (ω_P/ω_D) in the droplets are: (a) 1.68, (b) 1.94, (c) 2.44, (d) 2.97, (e) 4.03, (f) 5.08, (g) 6.18, (f) 7.25. Scale bars represent 200 μm.

Section 3. Relationship between the volume ratio of PEGDA-rich phase and DEX-rich phase (V_P/V_D) and the mass fraction ratio of PEGDA and DEX (ω_P/ω_D)

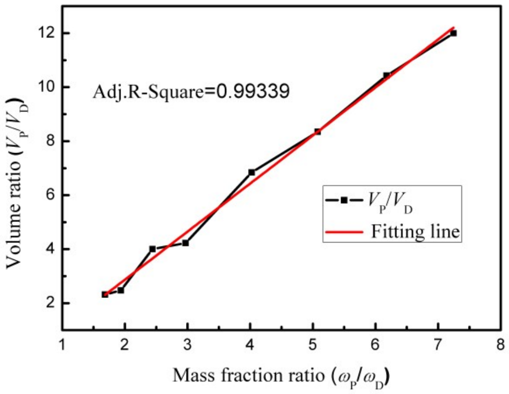

Figure S3. The diagram of the relationship between the volume ratio (V_P/V_D) and the mass ratio (ω_P/ω_D) in ATPS droplets.

Section 4. Component calculation of multi-phase system.

4.1 Calculation of the volume ratio (V_P/V_D) of the PEGDA-rich phase and the DEX-rich phase in the complex Janus droplet

A schematic diagram of a complex droplet with geometric parameters is shown in Figure S4. V_P is the volume of the PEGDA-rich phase in the aqueous droplet, V_D is the volume of the DEX-rich phase in the aqueous droplet, and other parameters V_j, V_i, r_i, r_P (equal to r_W), r_D, h_i, h_j, h_k are all defined in Figure S4.

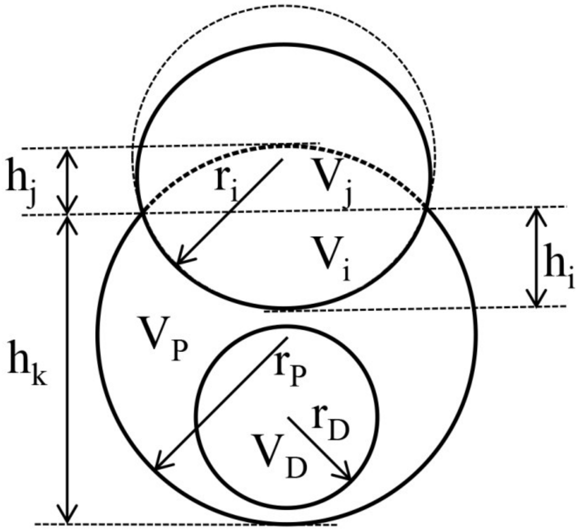

Figure S4. The schematic diagram of a complex Janus droplet with geometric parameters.

The calculation formulas for each part of the droplet are as follows:

$$V_j = \pi h_j^2 (r_p - \frac{h_j}{3}) = \pi (2r_p - h_k)^2 (r_p - \frac{2r_p - h_k}{3}) \tag{Eq.S1}$$

$$V_i = \pi h_i^2 (r_i - \frac{h_i}{3}) \tag{Eq.S2}$$

$$V_D = \frac{4}{3}\pi r_D^3 \tag{Eq.S3}$$

$$V_P = \frac{4}{3}\pi r_P^3 - V_i - V_j - V_D \tag{Eq.S4}$$

$$\frac{V_P}{V_D} = \frac{\frac{4}{3}\pi r_P^3 - V_i - V_j - V_D}{\frac{4}{3}\pi r_D^3} \tag{Eq.S5}$$

These can be applied to analyze the Effect of Flow Rate Ratio. As the flow ratio of oil phase to aqueous phase increases, the volume (V_W) of the water droplet decreases, and the volume (V_O) of the oil droplet increases. Based on mass transfer, the concentration (ω_P) of PEGDA in water droplets will increase, so is $\frac{\omega_P}{\omega_D}$. According to the phase relation (Figure S3), $\frac{V_P}{V_D}$ increases.

As $V_W = V_P + V_D$ decreases and $\frac{V_P}{V_D}$ increases, obviously, V_D is reduced and thus r_D decreases.

According to Eq S4, $\frac{4}{3}\pi r_P^3 = V_P + V_D + V_i + V_j = V_W + V_i + V_j$.

V_W decreases, but the value of $Vi + Vj$ increases as the degree of engulfment of oil droplets by water droplets increases. Therefore, r_W (rp) has no obvious trend of change, and it is roughly unchanged. The changes in the values of V_W, V_i and V_j can be obtained by actually measuring the droplet size (Figure 4a-e).

4.2. Calculation of the mass fraction of PEGDA (ω_P) and the mass fraction of DEX (ω_D) in the aqueous droplet of the complex Janus droplet

It has been known that $V_P/V_D = 1.779\ (\omega_P/\omega_D) - 0.6888$. The $V_P/V_D = 5.829$ is substituted to this formula and the result is:

$$\frac{\omega_P}{\omega_D} = 3.664$$

Assuming that the mass of PEGDA in the aqueous droplet is *a*, the mass of DEX is *b*, and the mass of water is *c*. Then

$$\frac{\omega_P}{\omega_D} = \frac{\frac{a}{a+b+c}}{\frac{b}{a+b+c}} = \frac{a}{b} = 3.664$$

Due to

$$\frac{b}{b+c} = 0.1$$

So

$$\omega_P = \frac{a}{a+b+c} = \frac{3.664b}{3.664b+10b} = 0.2681$$

$$\omega_D = \frac{b}{a+b+c} = \frac{b}{3.664b+10b} = 0.07319$$

4.3. Calculation of the mass fraction of PEGDA (ω_{PO}) and the mass fraction of ETPTA (ω_E) in the oil droplet of the complex Janus droplet

Assuming that the mass of PEGDA in the oil droplet is *d* and that of ETPTA is *e*. Since the flow rates of the oil phase and the aqueous phase are equal here, that is, one droplet is sheared to contain the same volume of the oil phase and the aqueous phase. Whereas the oil phase is a mixed solution of ETPTA (50 wt%) and PEGDA (50 wt%), which has a density of about 1.119 g/mL. The aqueous phase is the DEX aqueous solution with a mass fraction of 10wt% and a density of about 1.042 g/mL. So

$$\frac{e+d+a}{1.119} = \frac{b+c}{1.042}$$

$$\frac{a+d}{a+d+e}=0.5$$

Due to

$$\frac{b}{b+c}=0.1$$

$$\frac{a}{b}=3.664$$

From the above four equations, $e = 5.369b$ and $d = 1.705b$ are obtained. So,

$$\omega_{PO}=\frac{d}{d+e}=\frac{1.705b}{1.705b+5.369b}=0.2410$$

$$\omega_{E}=\frac{e}{d+e}=\frac{5.369b}{1.705b+5.369b}=0.7590$$

Section 5. Mechanism Analysis of Morphology Based on Interfacial Tensions

5.1 **Interfacial tensions (γ, mN/m) between liquid and liquid.** The morphology of complex emulsion droplets is controlled by interfacial tensions. Take the complex Janus droplets as an example, the continuous phase solution (CP Sol) is liquid paraffin containing 2 wt% EM 90. The solution of EPTTA (50 wt%) and PEGDA (50 wt%) was mixed with the DEX (10 wt%) aqueous solution. After standing, the solution was divided into three layers: the upper layer was PEGDA-rich phase solution (Sol I), the middle layer was ETPTA-rich phase solution (Sol II), and the lower layer was DEX-rich phase solution (Sol III). The solution of each layer was centrifuged at 5000 r/min for three minutes to obtain a clear solution of each layer. The interfacial tensions are measured (Table S1).

Table S1. Interfacial tensions (γ, mN/m) between liquid and liquid.

combination (Sol / Sol)	**symbol**	**value (mN/m)**
Sol I / CP Sol	$\gamma_{\text{P-R/C}}$	2.9
Sol II / CP Sol	$\gamma_{\text{E-R/C}}$	2.65
Sol III / CP Sol	$\gamma_{\text{D-R/C}}$	3.36
Sol I / Sol II	$\gamma_{\text{E-R/P-R}}$	0.65
Sol I / Sol III	$\gamma_{\text{P-R/D-R}}$	< 0.1
Sol II / Sol III	$\gamma_{\text{D-R/E-R}}$	2.77

5.2 **Interfacial tensions varies with the component contents.** The change of interfacial tension can be attributed to the compositions of droplet components (PEGDA, DEX), the content and type of surfactants in the continuous phase. The relationship between interfacial tension and component content was studied by using the pendant drop method. The interfacial tension ($\gamma_{P/C}$) between the aqueous solution of PEGDA with the continuous phase decreases as the PEGDA content increases (Figure S5a). The interfacial tension ($\gamma_{E/C}$) between the ETPTA solution containing PEGDA with the continuous phase increases as the PEGDA content increases (Figure S5a). Besides, the interfacial tension ($\gamma_{D/C}$) between the DEX aqueous solution and the continuous phase decreases as the DEX content increases (Figure S5b). Furthermore, the ETPTA solution containing PEGDA was mixed with water in an equal volume, and then divided into two layers after centrifuging, the upper layer was a PEGDA-rich phase aqueous solution, and the lower layer was an ETPTA-rich phase solution. The interfacial tension ($\gamma_{E\text{-}R/P\text{-}R}$) between the EPTTA-rich phase solution and the PEGDA-rich phase solution decreases as the initial PEGDA content (in the ETPTA solution before mixing) increases (Figure S5c). These results indicate that the interfacial tension changes significantly with the change of component concentration, which is the essence of morphology change.

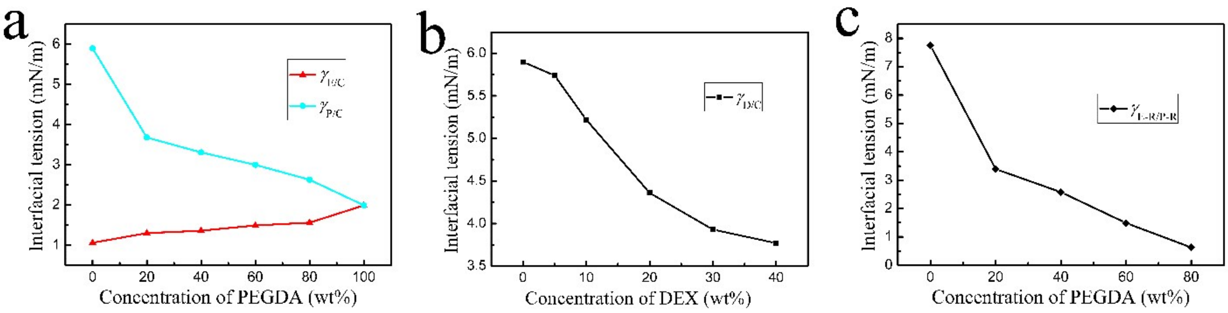

Figure S5. (a) The interfacial tensions between PEGDA aqueous solution and ETPTA solution and the continuous phase with the change of PEGDA concentrations. (b) The interfacial tensions between DEX aqueous solution and the continuous phase with the change of DEX concentrations. (c) The interfacial tension between ETPTA-rich phase and PEGDA-rich phase with the change of initial PEGDA concentration.

5.3 **Interfacial tensions without the EM90.** It is well known that surfactants can significantly reduce the interfacial tension. The droplets prepared with liquid paraffin containing 0 wt% EM 90 are taken as an example. The interfacial tensions are measured：$\gamma_{E\text{-}R/C} = 4.79$ mN/m, $\gamma_{P\text{-}R/C} = 10.24$ mN/m, $\gamma_{D\text{-}R/C} = 11.35$ mN/m. Obviously, each value is larger than the corresponding value (Table S1). $\gamma_{E\text{-}R/P\text{-}R}$ and $\gamma_{P\text{-}R/D\text{-}R}$ are unchanged. The morphology analysis of the complex emulsions can be described from oil-water droplet and DEX-PEGDA aqueous droplet (Table S2).

Since γ_O, γ_W and γ_{OW} match the inequality 2, the oil droplet completely engulfs the aqueous droplet to form a core/shell structure, which is consistent with the experimental phenomenon (Figure 7a). Since $\gamma_D > \gamma_P + \gamma_{DP}$, the

PEGDA-rich droplet completely engulfs the DEX-rich droplet, and forming a DEX/PEGDA core/shell droplet. This is consistent with the experimental phenomenon (Figure 7a).

Table S2. The interfacial tensions of the complex emulsions prepared with liquid paraffin containing 0 wt% EM 90.

	oil-water droplet			**aqueous droplet**		
	γ_O	γ_W	γ_{OW}	γ_P	γ_D	γ_{DP}
Value (mN/m)	4.79	10.24	0.65	10.24	3.36	< 0.1
relation	$\gamma_W > \gamma_O + \gamma_{OW}$			$\gamma_D > \gamma_P + \gamma_{DP}$		