

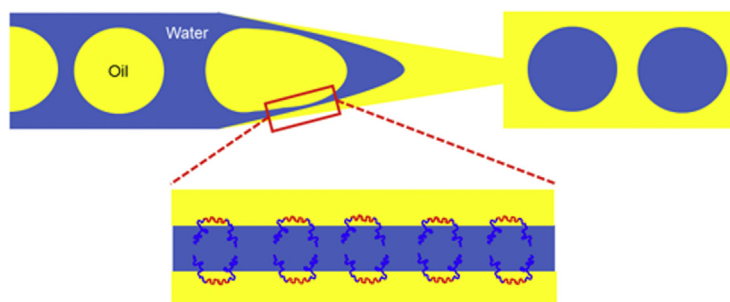
# Effect of triblock copolymer surfactant composition on flow-induced phase inversion emulsification in a tapered channel

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## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 26 August 2018

Revised 6 November 2018

Accepted 7 November 2018

Available online 8 November 2018

### Keywords:

Pluronic  
Emulsions  
Block copolymers  
Droplets  
Surfactants  
Microfluidics

## ABSTRACT

**Hypothesis:** Phase inversion emulsification (PIE) is a process that inverts the dispersed and continuous phases of an emulsion and is useful for preparing emulsions that are challenging to produce using conventional techniques. A recent work has shown that PIE can be induced by flowing an emulsion through a tapered channel. Although prior studies have shown that flow-induced PIE (FIPIE) is influenced by the flow conditions and wetting properties of the channel surface, little is known about the effect of surfactant structure on FIPIE. We hypothesize that FIPIE is affected by the composition and structure of the surfactant used for emulsion stabilization.

**Experiments:** We use Pluronics, a series of ABA triblock copolymers composed of hydrophilic poly(ethylene oxide) (PEO) and hydrophobic poly(propylene oxide) (PPO) with various lengths ( $A = \text{PEO}$ ,  $B = \text{PPO}$ ), as model surfactants to test this hypothesis. We observe that triblock copolymer surfactants with long PEO blocks suppress FIPIE. A scaling analysis based on a polymer brush model qualitatively agrees with the experimental observation. We also show that for small molecular weight Pluronics, FIPIE is significantly suppressed when Pluronics with large PPO blocks are used.

**Findings:** Our results strongly indicate that the steric repulsion provided by the PEO blocks as well as the dilatational elasticity provided by the PPO blocks are key factors that control the FIPIE process.

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## 1. Introduction

Emulsions are mixtures of two immiscible fluids, one dispersed in the other and are present in countless products and manufacturing processes of pharmaceuticals, cosmetics, and agriculture industries [1–3]. Conventional methods of emulsion generation

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typically involve highly energy intensive processes such as mechanical stirring and sonication which can be expensive and can potentially damage the final products due to undesirable heat generation [4–6].

Phase inversion emulsification (PIE) is a process that interconverts the dispersed and continuous phases of an emulsion and has been used to produce emulsions that are challenging to produce using conventional emulsification techniques [7–11]. Flow-induced phase inversion emulsification (FIPIE) is a process designed to achieve PIE by flowing a precursor emulsion through structured channels, potentially enabling continuous generation of target emulsions [12]. Prior reports have shown that an emulsion can undergo FIPIE as it flows through channels with barriers that promote the coalescence of the dispersed phase and encapsulation of the original continuous phase [13–15]. Other studies have demonstrated FIPIE by flowing emulsions through channels or membranes with preferable wettability towards the dispersed phases [16–19].

One of the key components that are added in the formation and stabilization of emulsions is a class of materials known as surface active agents (surfactants) such as amphiphilic molecules, copolymers, and solid particles [20–22]. Surfactants dwell at the interfaces between two immiscible fluids and lower the interfacial tension, facilitating the creation of interfaces and enhancing emulsion stability by providing electrostatic repulsion, steric repulsion, and/or increasing bulk and interfacial viscoelasticity [23–25].

Although several reports have focused on the development of FIPIE processes for emulsion generation, the effect of surfactant composition on the FIPIE of emulsions is not clearly understood. In this study, we focus on investigating the composition effect of polymeric surfactant, Pluronics, on the tendency of emulsions to undergo FIPIE. Pluronics are commercially available ABA triblock copolymers composed of hydrophilic poly(ethylene oxide) (PEO) and hydrophobic poly(propylene oxide) (PPO) (A = PEO, B = PPO) [26–28]. Pluronics provide an ideal system to study the effect of surfactant composition because a homologous series of the triblock copolymer surfactants are commercially available and widely used in the industrial processes and products. The tendency of emulsions to undergo FIPIE is analyzed using a recently developed FIPIE process that uses a tapered microchannel [29]. When an oil-in-water (O/W) emulsion is flowed through a hydrophobically treated tapered microchannel, oil droplets deform and undergo coalescence with an oil film on the surface of the channel, inducing phase inversion from O/W to water-in-oil (W/O) emulsions. The draining and rupture of the aqueous film between the oil phases in the phase inversion channel (PIC) depends strongly on the flow

conditions; emulsions tend to undergo FIPIE at a low velocity as they pass through the PIC. The use of a single tapered channel also provides important advantages of *in situ* monitoring and thus enables single droplet-level understanding of the phenomenon. Based on this approach, we find that the composition of the copolymer surfactants has a direct impact on the tendency of emulsions to undergo FIPIE and that the steric repulsion seems to be the major factor that influences the fate of emulsions flowing through PIC. Our findings on the effect of Pluronic composition on FIPIE provides guidance on surfactant selection for emulsion generation via FIPIE.

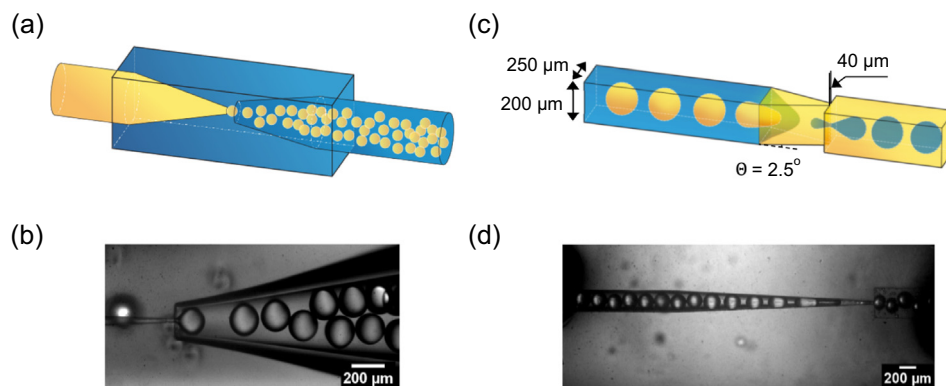
## 2. Materials and methods

### 2.1. Materials

10 Pluronics with different compositions are selected to make aqueous solutions with the concentration of 0.01 M. Their interfacial tensions and viscosities are measured using pendant drop tensiometry and Ubbelohde viscometry, respectively. The concentration of L64 and P65 is 0.05 M because emulsions formed with 0.01 M L64 and P65 are not stable enough to be used for FIPIE investigation. Fig. 1 shows the general steps involved in our study. An O/W precursor emulsion is first generated in a glass capillary device, and subsequently this emulsion is introduced into a hydrophobically modified polydimethylsiloxane (PDMS) PIC in which the precursor emulsion is flowed through a tapered channel. The channel width tapers from 250  $\mu\text{m}$  to 40  $\mu\text{m}$ , with an angle of 2.5°. The channel height is kept constant at 200  $\mu\text{m}$ . The FIPIE process is recorded with a high-speed camera.

### 2.2. Aqueous phase preparation and characterization.

Aqueous solutions with Pluronics (BASF) are prepared by dissolving corresponding surfactants in deionized (DI) water (18.2 m $\Omega$ -cm, purified by Barnstead Nanopure System). Light mineral oil (LMO, Fisher) is used as the oil phase. Interfacial tensions (IFT) between aqueous solutions and LMO are measured by pendant drop tensiometry using an optical tensiometer (Attention Theta). A pendant drop of LMO is formed in the aqueous polymer solution using a U-shape dispensing needle. The curvature of the oil droplet is recorded and analyzed to obtain IFT (OneAttention). The interface is allowed to equilibrate for an hour. The viscosities of the aqueous solutions of Pluronics are measured by using a Ubbelohde viscometer. A detailed procedure on using the Ubbelohde viscometer is included in the Supporting Information.



**Fig. 1.** Overview of precursor O/W emulsion generation and FIPIE processes. (a) Schematic illustration of precursor O/W emulsion generation in a glass capillary device. The aqueous and oil phases are presented in blue and yellow, respectively. (b) Optical microscope image of precursor O/W emulsion generation. (c) Schematic illustration of O/W to W/O FIPIE process in a tapered channel. The channel width tapers from 250  $\mu\text{m}$  to 40  $\mu\text{m}$  with an approach angle of  $\theta = 2.5^\circ$ . The channel height is 200  $\mu\text{m}$ . (d) Optical microscope image of O/W to W/O FIPIE process in a tapered channel. The water phase contains methylene blue, imparting contrast between the two liquid phases.

### 2.3. Precursor oil-in-water emulsion preparation

Precursor O/W emulsions are prepared using a glass capillary device. Fabrication of the glass capillary device has been described elsewhere [29–30]. Briefly, aqueous and oil phases are introduced into the device using syringe pumps (Harvard Apparatus). The flow rates are kept at 100–500  $\mu\text{L/hr}$  and 600–2000  $\mu\text{L/hr}$  for the oil and aqueous phases, respectively. Uniform 200  $\mu\text{m}$  diameter O/W emulsions are prepared with methylene blue added to the aqueous phase to facilitate visualization under an optical microscope (Fig. 1).

### 2.4. Flow-induced phase inversion emulsification (FIPIE)

The precursor O/W emulsions are stored in vertically oriented polyethylene tubing for 1 h. The creamed dispersed oil droplets are subsequently introduced into a PDMS PIC device to study FIPIE. Fabrication of the PDMS device has been described elsewhere [29]. The PIC channel height is 200  $\mu\text{m}$ . In our previous study [29], we found phase inversion in the PIC does not take place if the approach angle of the channel is higher than  $5^\circ$ , or if the ratio of droplet size and channel width is less than 2. Consequently, in this study, we adopt a channel with an approach angle of  $2.5^\circ$  (Fig. 1) to study the effect of the composition of Pluronics on FIPIE, and the size of droplets are kept at 200  $\mu\text{m}$  to ensure that they are significantly deformed within the tapered channel. The channel surface is hydrophobically modified with octadecyltrichlorosilane (OTS, Sigma) and pretreated with LMO before injection of the precursor emulsions. The tubing with creamed precursor emulsions is reconnected to glass syringe (SGE Analytical Science, Trajan Scientific & Medical) containing corresponding aqueous phases, and the emulsions are injected into the PDMS devices at flow rates between 20  $\mu\text{L/hr}$  and 2000  $\mu\text{L/hr}$  using a syringe pump (Harvard Apparatus). The velocity of each droplet is tracked by measuring the displacement of the oil droplet centroid, using images captured under an inverted microscope (Nikon Exlipse TE200) equipped with a high-speed camera (Phantom v7.1). Videos are recorded at the frame rates ranging between 10 and 100 frames per second. The ImageJ software package is used to process images and measure the distances traveled by droplets in the last 10 to 100 frames before their point of FIPIE or before they flow out of the tapered channel without FIPIE.

### 2.5. Interfacial dilatational elasticity measurement

The interfacial dilatational elasticity is measured using pendant drop tensiometry using the same set-up as that used in the aforementioned IFT measurement. The oil-water interface is created by dispensing a 5  $\mu\text{L}$  LMO droplet into an aqueous polymer solution using a U-shape dispensing needle. The droplet volume is sinusoidally oscillated to a maximum change of 10% of its original volume. The oscillating frequency is 0.01 Hz. The concentration of Pluronic solutions are 1  $\mu\text{M}$ . The dynamic change in the shape of the LMO droplet is recorded and analyzed to obtain IFT and dilatation elasticity (OneAttention).

## 3. Results

The effect of surfactant composition on FIPIE is investigated by examining the percentage of the precursor emulsion droplets that undergo FIPIE under a given set of conditions. The precursor emulsion is first generated in a glass capillary microfluidic device then introduced into a tapered PDMS channel as illustrated in Fig. 1. The FIPIE of individual droplets is closely monitored under an inverted microscope.

To understand the effect of surfactant composition on the tendency of emulsion droplets to undergo FIPIE, we vary the molecular weight (MW) as well as the ratio of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) segments of the Pluronics. 10 Pluronics are selected which can be grouped in different ways to probe the effect of various aspects of surfactant compositions and structures on FIPIE. The composition and molecular weight of the 10 Pluronics are summarized in Table 1 [26–28].

Unless noted otherwise, we use aqueous solutions that have 0.01 M Pluronics, which is significantly higher than the critical micelle concentrations of the polymers. Discussion on possible effect of Pluronics concentration on FIPIE is provided in the Supporting Information. To test and understand how the composition of surfactants may affect the tendency of emulsions to undergo FIPIE in the PIC, we attempt to plot the frequency of FIPIE as a function of a control variable. One dimensionless number that could be used as the variable is Capillary (Ca) number:

$$\text{Ca} = \frac{\mu_c \cdot v}{\gamma} \quad (1)$$

where  $\mu_c$  is the dynamic viscosity of the continuous phase,  $v$  is the velocity of the emulsion extrapolated from droplet centroid displacement, and  $\gamma$  is the interfacial tension between the continuous and dispersed phases. Ca represents the relative importance of viscous force to the interfacial tension force and is widely used to understand dynamic fluid phenomena at small scales where the viscous forces dominate over the inertial forces [31]. Another possibility is the product of Capillary number (Ca) and viscosity ratio ( $\lambda$ ), which is defined as the dynamic viscosity ratio between that of the dispersed phase ( $\mu_d$ ) and continuous phase ( $\mu_c$ ):

$$\lambda = \frac{\mu_d}{\mu_c} \quad (2)$$

A recent study showed a strong correlation between break-up probability of a concentrated emulsion passing through a constricted channel and  $\text{Ca} \cdot \lambda$  [32]. In this reference, the break-up profiles of the emulsions with different viscosity ratios collapse onto a single curve when  $\text{Ca} \cdot \lambda$  is used as the variable, which demonstrated that the viscosity of the droplet, which represents the resistance of the droplet against shape change under compression, is the determining factor for emulsion break-up.

**Table 1**  
Pluronics used in this work.

Pluronic <sup>a</sup>	MW <sup>b</sup>	PEO% <sup>c</sup>	$n_{\text{PEO}}$ <sup>d</sup>	$n_{\text{PPO}}$ <sup>e</sup>
L64	2900	40%	$2 \times 13$	30
P65	3400	50%	$2 \times 18$	29
F68	8400	80%	$2 \times 76$	29
F77	6600	70%	$2 \times 53$	34
P84	4200	40%	$2 \times 19$	43
F88	11,400	80%	$2 \times 103$	39
P104	5900	40%	$2 \times 27$	61
F108	14,600	80%	$2 \times 132$	50
P123	5750	30%	$2 \times 19$	69
F127	12,600	70%	$2 \times 100$	65

<sup>a</sup> The nomenclature of Pluronics is composed of one letter followed by a 2–3-digit numeric code. The letter being either F, P, or L, stands for flakes, paste, or liquid. The one to two digits following the letter represent 1/300 of the molar mass of the PPO block of the Pluronics. The last digit represents one-tenth of the molar mass percentage of the PEO blocks of the Pluronics. For example, the molar mass percentage of PEO in F108 is 80%, and its PPO block molar mass is around  $10 \times 300 = 3000$  (2920) Da [26,28].

<sup>b,c</sup> Molecular weight and PEO% are provided by the supplier, BASF.

<sup>d</sup>  $n_{\text{PEO}}$  represents the number of PEO units in a single PEO block. The average number of  $n_{\text{PEO}}$  were calculated using the MW and PEO%.

<sup>e</sup>  $n_{\text{PPO}}$  represents the number of PPO units in the PPO block. The average number of  $n_{\text{PPO}}$  were calculated using MW and PEO%.

In our analysis, however, a universal curve does not emerge when the frequencies of FIPIE of emulsions prepared using different Pluronics are plotted using  $Ca$ ,  $Ca \cdot \lambda$  or even using the linear velocity of droplets through PIC as the control variable. The absence of a universal behavior prompts us to hypothesize that the surfactant structure could be an important factor that must be considered since these variables do not consider the molecular details of the interface. As mentioned above, because of the high viscosity of the dispersed phase, we decide to use  $Ca \cdot \lambda$  as the control variable. This parameter also gives the most consistent trends in the frequencies of FIPIE as a function of MW,  $\eta_{PEO}$ , and  $\eta_{PPO}$  as will be discussed below. The FIPIE trends remain the same when the velocity of the emulsion is used as the variable.

The phase inversion frequency for an emulsion passing through the PIC is estimated based on the percentage of at least 30 droplets that undergo FIPIE:[29]

$$\text{FIPIE Frequency} = \frac{\# \text{ of droplets that undergo FIPIE}}{\# \text{ of droplets that pass through the PIC}} \quad (3)$$

The frequency of FIPIE as a function of  $Ca \cdot \lambda$  show profiles that can be described by a modified logistic function:

$$y(x) = \frac{(x)^k}{(x)^k + (x_0)^k} \quad (4)$$

A detailed derivation is included in the Supporting Information.

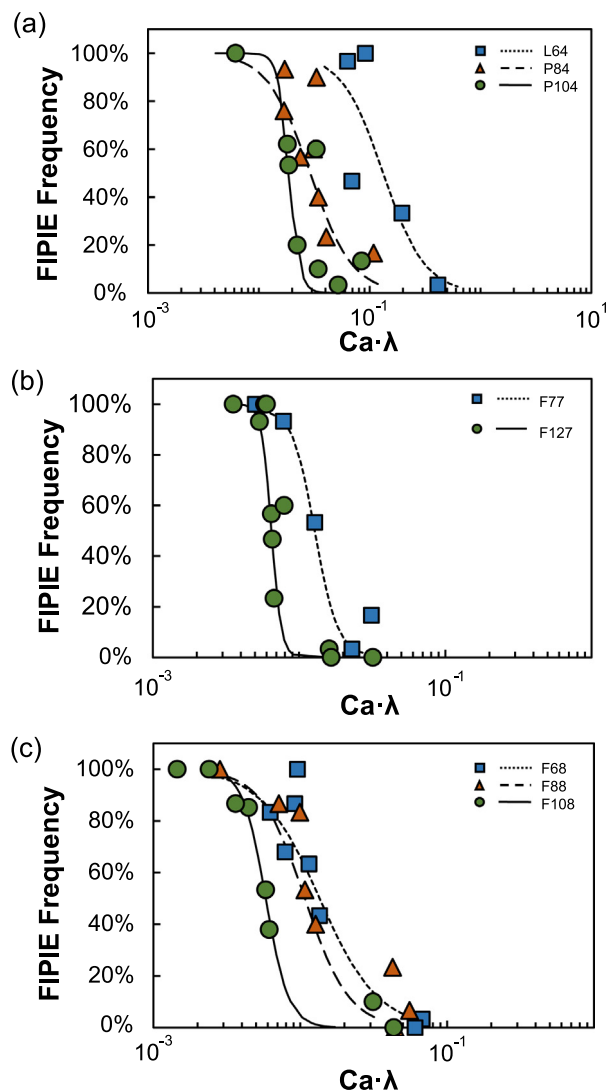
When droplets fail to undergo FIPIE, oil-in-water-in-oil (O/W/O) multiple emulsions are generated. The number of the inner droplets present in the resulting multiple emulsions depend on the FIPIE frequency. Emulsions with multiple number of inner droplets are more frequently generated at a low FIPIE frequency. The number of the inner droplets in the resulting emulsions decreases and eventually disappears as the FIPIE frequency increases from 0% to 100%.

### 3.1. Effect of molecular weight (MW) of triblock copolymers on FIPIE

To test the effect of molecular weight (MW) of the block copolymer, three sets of Pluronics at different PEO% with increasing MW are compared. In the increasing order of MW, Set 1-1 comprise MW = 2900, 4200, 5900: L64 < P84 < P104; Set 1-2: MW = 6600, 12,600: F77 < F127; Set 1-3: MW = 8400, 11,400, 14,600: F68 < F88 < F108 (Table 2). All FIPIE profiles have similar shapes that can be described by logistic functions, with FIPIE frequency decreasing from 1 to 0 with increasing  $Ca \cdot \lambda$  as seen in Fig. 2. Emulsions that can sustain lower  $Ca \cdot \lambda$  without undergoing FIPIE are more resistant to FIPIE. Thus, a leftward shift in FIPIE profiles with increasing of MW observed in Fig. 2 suggests decreased tendency of emulsions to undergo FIPIE, or increased stability of emulsions against FIPIE with an increase in the MW of Pluronics. With increasing MW of the surfactant, the transition from no FIPIE to complete FIPIE becomes steeper (i.e., higher absolute value of  $k$ ),

**Table 2**  
Pluronics used in analyzing effect of MW of triblock copolymers on FIPIE.

Set	Pluronic	MW	PEO%	$\eta_{PEO}$	$\eta_{PPO}$
1-1	L64	2900	40%	$2 \times 13$	30
	P84	4200	40%	$2 \times 19$	43
	P104	5900	40%	$2 \times 27$	61
1-2	F77	6600	70%	$2 \times 53$	34
	F127	12,600	70%	$2 \times 100$	65
1-3	F68	8400	80%	$2 \times 76$	29
	F88	11,400	80%	$2 \times 103$	39
	F108	14,600	80%	$2 \times 132$	50



**Fig. 2.** FIPIE frequency of O/W emulsions in PICs as a function of  $Ca \cdot \lambda$ , for sets of Pluronics with constant  $\eta_{PEO}/\eta_{PPO}$  and increasing MW. (a) Set 1-1: 40% PEO Pluronics with MW in the order of L64 < P84 < P104; (b) Set 1-2: 70% PEO Pluronics with MW in the order of F77 < F127; (c) Set 1-3: 80% PEO Pluronics with MW in the order of F68 < F88 < F108.

suggesting a more sudden transition in the FIPIE profiles for Pluronics with higher MW (see Table S1 in Supplemental Information).

### 3.2. Effect of PEO length on FIPIE

We probe the effect of the length of PEO blocks while keeping the length of PPO blocks constant to isolate and analyze the effect of  $\eta_{PEO}$  (length of PEO) on FIPIE using three sets of Pluronics. In the increasing order of  $\eta_{PEO}$ , Set 2-1:  $\eta_{PEO} = 13, 18, 76$ : L64 < P65 < F68; Set 2-2:  $\eta_{PEO} = 19, 103$ : P84 < F88; Set 2-3:  $\eta_{PEO} = 27, 132$ : P104 < F108 (Table 3). The FIPIE profiles shift uniformly leftwards with increase of  $\eta_{PEO}$ , indicating that emulsion's tendency to undergo FIPIE decreases with an increase in  $\eta_{PEO}$  (Fig. 3).

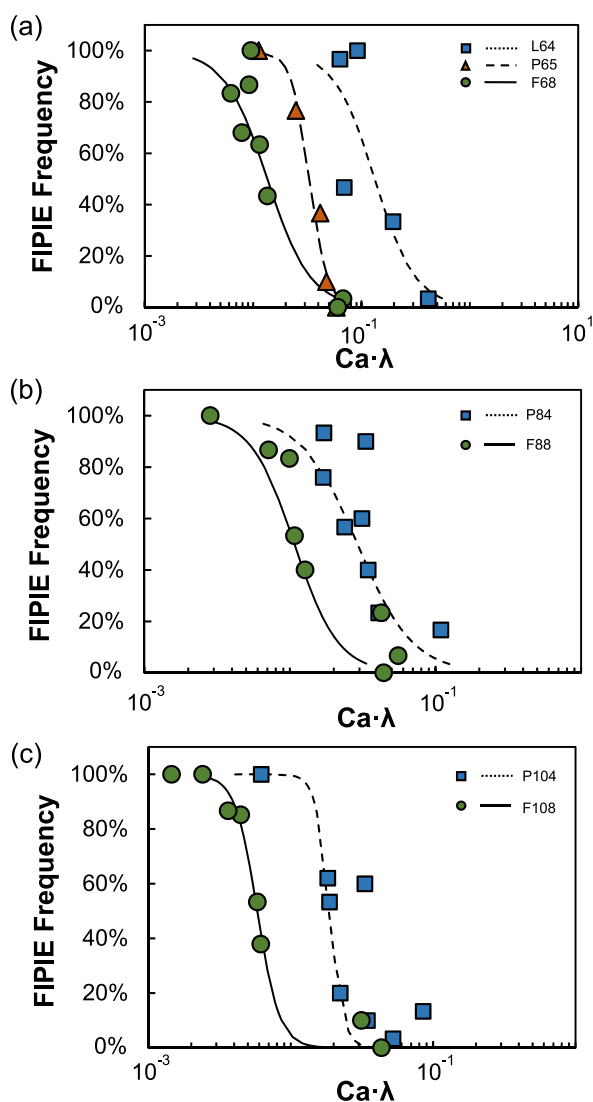
### 3.3. Effect of PPO length on FIPIE

Here we study the effect of the length of PPO blocks while keeping the length of PEO blocks constant to isolate and analyze the effect of  $\eta_{PPO}$  (length of PPO) on FIPIE using two sets of Pluronics.



**Table 3**  
Pluronics used in analyzing effect of  $n_{\text{PEO}}$  of triblock copolymers on FIPIE.

Set	Pluronic	MW	PEO%	$n_{\text{PEO}}$	$n_{\text{PPO}}$
2-1	L64	2900	40%	$2 \times 13$	30
	P65	3400	50%	$2 \times 18$	29
	F68	8400	80%	$2 \times 76$	29
2-2	P84	4200	40%	$2 \times 19$	43
	F88	11,400	80%	$2 \times 103$	39
2-3	P104	5900	40%	$2 \times 27$	61
	F108	14,600	80%	$2 \times 132$	50



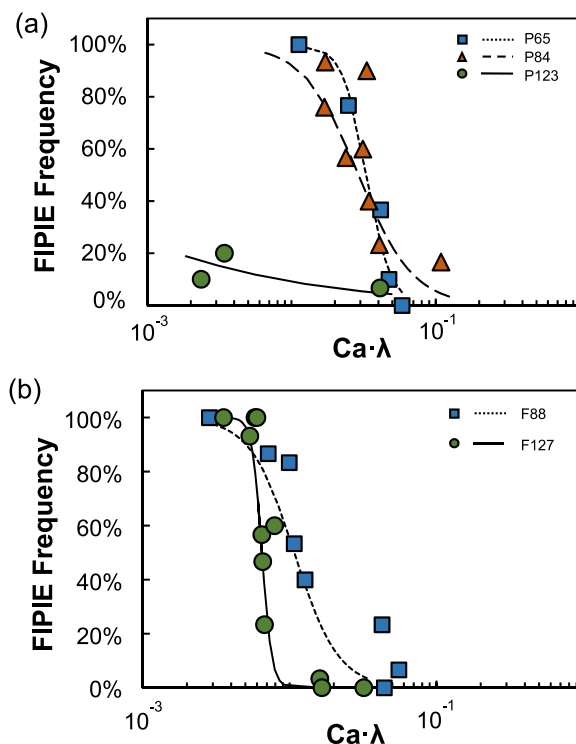
**Fig. 3.** FIPIE frequency of O/W emulsions in PICs as a function of  $\text{Ca} \cdot \lambda$ , for sets of Pluronics with constant  $n_{\text{PPO}}$  and increasing  $n_{\text{PEO}}$ . (a) Set 2-1:  $n_{\text{PEO}}$  in the order of L64 < P65 < F68; (b) Set 2-2:  $n_{\text{PEO}}$  in the order of P84 < F88; (c) Set 2-3:  $n_{\text{PEO}}$  in the order of P104 < F108.

In the increasing order of  $n_{\text{PPO}}$ , Set 3-1:  $n_{\text{PPO}} = 29, 43, 69$ : P65 < P84 < P123; Set 3-2:  $n_{\text{PPO}} = 39, 65$ : F88 < F127 (Table 4).

Interestingly, the FIPIE frequency profiles for P65 and P84 are quite similar, whereas the P123 stabilized emulsions exhibit dramatic resistance against FIPIE despite their similar  $n_{\text{PEO}}$ ; 100% FIPIE cannot be achieved when emulsions are stabilized with P123 even at very low values of  $\text{Ca} \cdot \lambda$  (Fig. 4). In the meantime, the Set 3-2 FIPIE profiles shift leftwards with increase of  $n_{\text{PPO}}$ . We discuss the potential reasons behind these tendencies below.

**Table 4**  
Pluronics used in analyzing effect of  $n_{\text{PPO}}$  of triblock copolymers on FIPIE.

Set	Pluronic	MW	PEO%	$n_{\text{PEO}}$	$n_{\text{PPO}}$
3-1	P65	3400	50%	$2 \times 18$	29
	P84	4200	40%	$2 \times 19$	43
	P123	5750	30%	$2 \times 19$	69
3-2	F88	11,400	80%	$2 \times 103$	39
	F127	12,600	70%	$2 \times 100$	65



**Fig. 4.** FIPIE frequency of O/W emulsions in PICs as a function of  $\text{Ca} \cdot \lambda$ , for sets of Pluronics with constant  $n_{\text{PEO}}$  and increasing  $n_{\text{PPO}}$ . (a) Set 3-1:  $n_{\text{PPO}}$  in the order of P65 < P84 < P123; (b) Set 3-2:  $n_{\text{PPO}}$  in the order of F88 < F127. P123 curve is an aid for the eye rather than a fit to a logistic function.

#### 4. Discussion

These results show that surfactant composition strongly affects the tendency of an emulsion to undergo FIPIE. The FIPIE tendency of Pluronic-stabilized emulsions consistently show negative correlation with  $n_{\text{PEO}}$  as seen by the leftward shift of FIPIE profiles when an emulsion is stabilized with triblock copolymers with longer PEO blocks. This trend could originate from the conformation of the triblock copolymer at the oil-water interface. Prior studies on the behavior of Pluronics at the oil-water interface have reported that PEO blocks form brush-like layers that stretch into the aqueous phases, providing steric repulsion between approaching oil-water interfaces [33–34]. With an increase in the  $n_{\text{PEO}}$ , the thickness of the resulting brush layer increases, strongly suggesting that the tendency of emulsion droplets to undergo FIPIE depends on the strength of repulsive steric interactions provided by the hydrophilic domain of the copolymer surfactant.

It was previously shown that a critical step that leads to the FIPIE of an emulsion in a tapered channel is the drainage and rupture of an aqueous film between an oil droplet and a wetting layer of oil on the channel surface as the droplet passes through the tapered channel [18,29]. As the oil droplet is deformed, the aqueous film is thinned and eventually this film destabilizes, leading

to film rupture and phase inversion of the emulsion. We hypothesize that the rupture of this aqueous film is correlated with the so-called driving pressure which is the difference between capillary pressure and the disjoining pressure: [35–38]

$$\Delta P = P_{\sigma} - \Pi \quad (5)$$

where  $\Delta P$  is the driving pressure,  $P_{\sigma}$  is the capillary pressure across the fluid interface, and  $\Pi$  is the disjoining pressure. The driving pressure determines whether drainage of a fluid film would take place as well as the rate of liquid drainage from the film.

The disjoining pressure,  $\Pi$ , is a combination of thermodynamic forces that act upon a liquid film, including van der Waals (vdW) attraction, steric repulsion, and electrostatic interaction, and can be expressed as: [39–41]

$$\Pi = \Pi_{\text{vdW}} + \Pi_{\text{steric}} + \Pi_{\text{elec}} \quad (6)$$

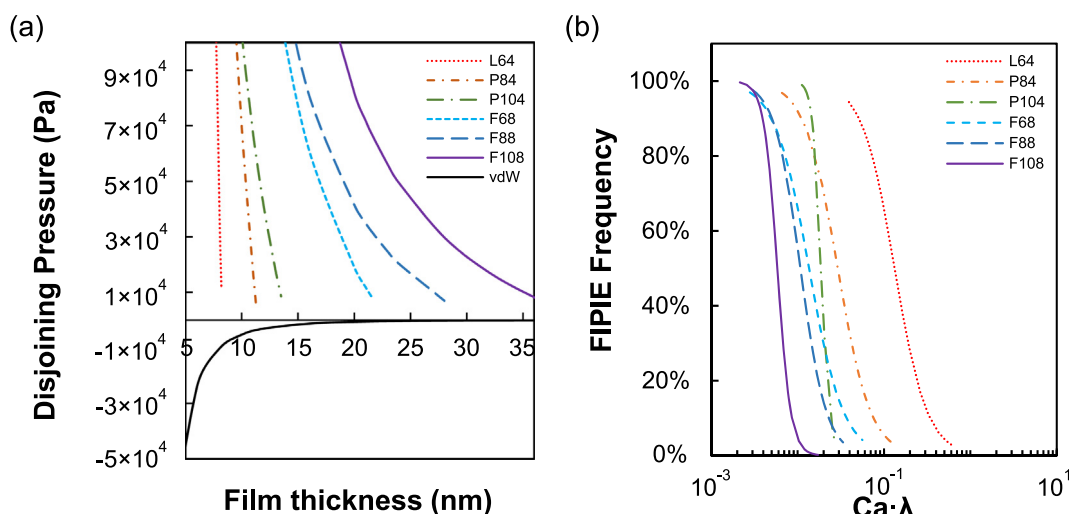
We hypothesize that the tendency of emulsions to undergo FIPIE depends strongly on steric repulsion pressure which decreases driving pressure for thinning of the aqueous film and suppresses the reduction in the film thickness. Electrostatic

contribution to the disjoining pressure is likely to be negligible in the current system since Pluronic is a non-ionic surfactant. Steric pressure from a brush layer can be estimated based on the Alexander-de Gennes brush model: [34,42–43]

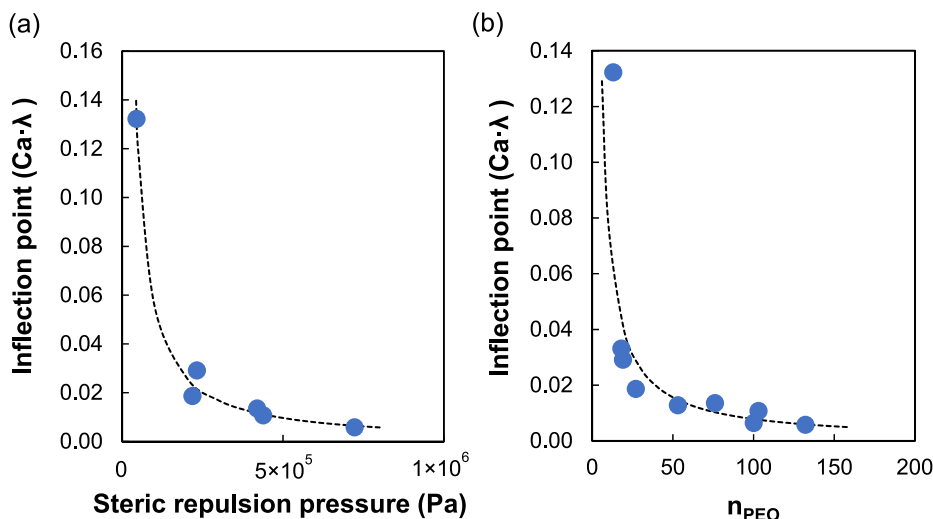
$$\Pi_{\text{steric}} = \alpha \frac{k_B T}{s^3} \left[ \left( \frac{2\delta}{h} \right)^{9/4} - \left( \frac{h}{2\delta} \right)^{3/4} \right] \text{ at } 0 < 2\delta < h \quad (7)$$

$$\Pi_{\text{steric}} = 0 \text{ at } 2\delta \geq h$$

where  $\alpha$  is empirically fitted parameter,  $s$  is the average distance between anchor points of PEO blocks at the water-oil interface,  $\delta$  is the brush layer thickness, and  $h$  is the thickness of the thin film. The steric pressure provided by different triblock copolymer surfactants are calculated as shown in Fig. 5. A detailed procedure for estimating the steric disjoining pressure is described in the Supporting Information. For a given aqueous film thickness, the vdW attraction stays constant, whereas steric repulsion pressure increases with molecular weight and  $n_{\text{PEO}}$ , lowering the total driving pressure for aqueous film drainage, and increasing the resistance of the emulsion against FIPIE. This trend (Fig. 5a) is consistent with the



**Fig. 5.** (a) van der Waals (vdW shown in the black solid curve) attraction, steric repulsion of 6 Pluronic, L64, P84, P104, F68, F88, and F108, calculated as a function of aqueous film thickness (b) FIPIE profile of the 6 Pluronic.



**Fig. 6.** FIPIE profile inflection points plotted as a function of (a) the steric repulsion pressure provided by Pluronic, steric pressures calculated at aqueous film thickness of 8 nm for L64, P84, P104, F68, F88, and F108, and of (b) the  $n_{\text{PEO}}$  of all Pluronic used in this study except P123.

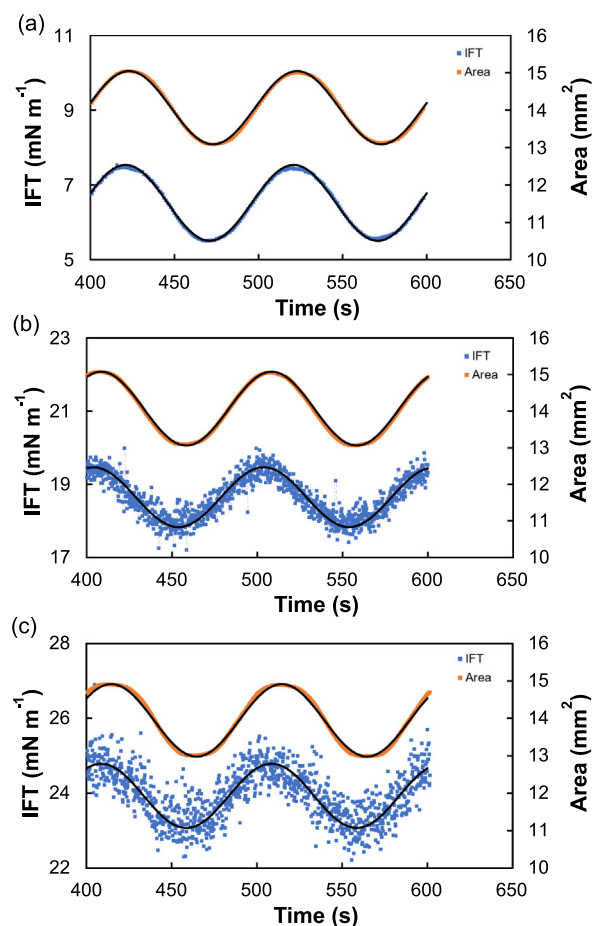
resistance of emulsions to undergo FIPIE as summarized in Fig. 5b, and thus strongly supports the hypothesis that larger Pluronics and longer PEO are able to resist FIPIE by providing stronger steric repulsions between oil droplets and oil layers on the channel surface. Although our experimental system does not satisfy all of the assumptions behind the Alexander-de Gennes brush model, the consistency in the FIPIE trend and steric pressures provided by Pluronics offers us an important insight into the role of steric repulsions in film rupture in dynamic flow conditions. Also our pressure analysis is based on equilibrium models; however, the dynamic adsorption of the surfactant could have important effects on the FIPIE behavior. Further analysis would be needed for deeper understanding of the effect of dynamic adsorption of Pluronics during droplet deformation.

The inflection points of the FIPIE profiles also show a power law correlation with the steric repulsion pressures provided by the Pluronics as shown in Fig. 6a. This trend indicates that while there is a strong inverse correlation between the steric repulsion pressure and the length of PEO in determining the tendency of emulsions to undergo FIPIE, with an increase in the PEO%, the MW effect on FIPIE suppression diminishes. For the Set 1-1, Pluronics with 40% PEO, the inflection points shifted leftwards by 0.1136 as the MW increases from 2900 Da (L64) to 5900 Da (P104). Comparatively, for the Set 1-3, Pluronics with 80% PEO, the inflection points shifted leftwards by only 0.0077 as the MW increases from 8400 Da (F68) to 14,600 Da (F108).

One interesting possibility is whether increasing the molecular weight of Pluronic while keeping the ratio of PEO and PPO lengths constant has the same impact on FIPIE as increasing the molecular weight of Pluronic by simply increasing the PEO length only. This question can be answered by comparing the results from Sets 1 and 2. Pluronics in Set 1 have increasing MWs with constant ratios of  $n_{\text{PEO}}:n_{\text{PPO}}$ . Pluronics in Set 2 have increasing PEO block length with a constant PPO block length; thus the MW of the polymer as well as the ratio of  $n_{\text{PEO}}$  and  $n_{\text{PPO}}$  change. To test whether the trend observed for Set 2 has the same trend as Set 1, we plot the inflection points of the two sets as a function of MWs (Figure S2). The exponents of the power laws are different, suggesting that the changing  $n_{\text{PEO}}$  has different effect than increasing the total MW while keeping the ratio of  $n_{\text{PEO}}$  and  $n_{\text{PPO}}$  constant.

Meanwhile, P123-stabilized emulsions exhibit a unique behavior when they are compared to those stabilized with Pluronics with similar  $n_{\text{PEO}}$  but different  $n_{\text{PPO}}$ . Emulsions made with P123 show extraordinarily high resistance against FIPIE; FIPIE frequency was suppressed to under 20% for the entire range of  $\text{Ca} \cdot \lambda$  we explored. While we do not fully understand the mechanism behind such high resistance against FIPIE, one possibility is that the high stability originates from the long PPO block of P123 compared to P84 and P65. The PPO blocks can dwell at the fluid interface thus provide high dilatational elasticity leading to high resistance against rupture of the aqueous film during large deformation of the emulsion interface. Prior studies have in fact shown that emulsions with increased dilatational elasticity have higher emulsion stability, consistent with our results [44–45].

To test this hypothesis, we use the oscillating pendant drop method to probe the interfacial rheology of Pluronic-covered oil-water interfaces. The dynamic changes of area and IFT of a sinusoidally oscillated pendant drop are recorded (Fig. 7), from which the storage modulus ( $E'$ ) at the interface can be derived. The P123 provides the highest storage modulus, 14.22 mN/m, whereas the storage modulus provided by P84 and P65 are 10.29 and 10.88 mN/m respectively (Table 5). The phase angle between the area and IFT curves also increase from 7.17° of P123 to 16.93° of P84 and 20.45° of P65, implying the interfaces becoming more viscous and less elastic. Equations used for the dilatational elasticity calculation are provided in the Supporting Information.



**Fig. 7.** Interfacial area and interfacial tension changes induced by sinusoidally oscillating an LMO oil pendant drop in contact with (a) P123, (b) P84, and (c) P65 aqueous solutions. The concentrations of the Pluronics are kept at 1  $\mu\text{M}$ . The oscillating frequency is 0.01 Hz.

**Table 5**  
Interfacial moduli of P123, P84, and P65 covered oil-water interface.

	Storage modulus ( $E'$ (mN m <sup>-1</sup> ))	Loss modulus ( $E''$ (mN m <sup>-1</sup> ))	Phase angle ( $\delta$ (°))
P123	14.22	1.79	7.17
P84	10.29	3.11	16.93
P65	10.88	4.07	20.45

The difference between the FIPIE profiles of F88 and F127 is relatively small compared to that among P65, P84 and P123. This can possibly be due to their MW. The MW of F88 and F127 are much larger (>10,000 Da) compare to that of P65, P84, and P123 (<6000 Da).

## 5. Conclusions

In this work, we provide a comprehensive investigation of the effect of Pluronic composition and molecular weight on the FIPIE of emulsions in a tapered channel. Although prior reports have described phase inversion emulsifications using microfluidics [14–15,17,19,29], most of these papers have focused on studying the effect of surface wettability and hydrodynamic conditions on phase inversion emulsifications. To our best knowledge, our work is the first to address how the structure of surfactants affect

flow-induced phase inversion emulsification using a microfluidic approach. We test our hypothesis that molecular structure of surfactants would affect the FIPIE behavior of droplets flowing through a tapered channel by using triblock copolymer surfactant, Pluronics. Our results show a negative correlation between Pluronic  $\eta_{PEO}$  and the tendency of emulsions to undergo FIPIE. A scaling analysis suggests that upon compression, the brush layer formed by the hydrophilic domain of PEO-PPO-PEO copolymer surfactants at the interfaces provide high steric repulsion, suppressing the drainage of the thin aqueous film and the coalescence of the oil droplet and the oil layer on the channel surface. These effects subsequently hinder FIPIE. A drastic suppression of the FIPIE by a small molecular weight, high PPO% Pluronic, P123, is also observed, which we attribute to the dilatational elasticity provided by its PPO block at the oil/water interface. We believe the understanding obtained in this work will potentially promote broader application of FIPIE, reducing emulsification energy cost and enabling continuous processing of emulsions for materials fabrications [12,29,46]. Our results provide important guidance on the selection of surfactants to control FIPIE. Future studies are warranted to generalize the conclusions of this study to other surfactants.

### Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Acknowledgements

This work was supported by NSF – 1604536. The authors also thank BASF for generously providing Pluronics used in this study.

### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2018.11.014>.

### References

- [1] S. Varona, S. Kareth, Á. Martín, M.J. Cocero, Formulation of lavandin essential oil with biopolymers by PGSS for application as biocide in ecological agriculture, *J. Supercrit. Fluids* 54 (3) (2010) 369–377.
- [2] M.N. Yukuyama, D.D.M. Ghisleni, T.J.A. Pinto, N.A. Bou-Chacra, Nanoemulsion: process selection and application in cosmetics – a review, *Int. J. Cosmet. Sci.* 38 (1) (2015) 13–24.
- [3] E. Bouyer, G. Mekhloufi, V. Rosilio, J.L. Grossiord, F. Agnely, Proteins, polysaccharides, and their complexes used as stabilizers for emulsions: alternatives to synthetic surfactants in the pharmaceutical field?, *Int. J. Pharm.* 436 (1–2) (2012) 359–378.
- [4] R. Petela, Generation of oil emulsion for stirred tank processes, *Fuel* 73 (4) (1994) 557–562.
- [5] N. Sadurni, C. Solans, N. Azemar, M.J. Garcia-Celma, Studies on the formation of O/W nano-emulsions, by low-energy emulsification methods, suitable for pharmaceutical applications, *Eur. J. Pharm. Sci.: Off. J. Eur. Fed. Pharm. Sci.* 26 (5) (2005) 438–445.
- [6] V. Karcher, F.A. Perrechil, A.C. Bannwart, Interfacial energy during the emulsification of water-in-heavy crude oil emulsions, *Braz. J. Chem. Eng.* 32 (2015) 127–137.
- [7] S. Sajjadi, Nanoemulsion formation by phase inversion emulsification: on the nature of inversion, *Langmuir ACS J. Surfaces Colloids* 22 (13) (2006) 5597–5603.
- [8] Z.Z. Yang, Y.Z. Xu, D.L. Zhao, M. Xu, Preparation of waterborne dispersions of epoxy resin by the phase-inversion emulsification technique. 1. Experimental study on the phase-inversion process, *Colloid Polym. Sci.* 278 (12) (2000) 1164–1171.
- [9] J.L. Salager, A. Forgiarini, L. Marquez, A. Pena, A. Pizzino, M.P. Rodriguez, M. Rondon-Gonzalez, Using emulsion inversion in industrial processes, *Adv. Colloid Interface Sci.* 108–109 (2004) 259–272.
- [10] F. Bouchama, G.A. van Aken, A.J.E. Autin, G.J.M. Koper, On the mechanism of catastrophic phase inversion in emulsions, *Colloids Surf. A* 231 (1–3) (2003) 11–17.
- [11] A. Perazzo, V. Preziosi, S. Guido, Phase inversion emulsification: Current understanding and applications, *Adv. Colloid Interface Sci.* 222 (2015) 581–599.
- [12] A. Kumar, S. Li, C.-M. Cheng, D. Lee, Recent Developments in Phase Inversion Emulsification, *Ind. Eng. Chem. Res.* 54 (34) (2015) 8375–8396.
- [13] G. Akay, Flow-induced phase inversion in the intensive processing of concentrated emulsions, *Chem. Eng. Sci.* 53 (2) (1998) 203–223.
- [14] N. Bremond, H. Domejean, J. Bibette, Propagation of drop coalescence in a two-dimensional emulsion: a route towards phase inversion, *Phys. Rev. Lett.* 106 (21) (2011) 214502.
- [15] N. Bremond, A. Thiam, J. Bibette, Decompressing Emulsion Droplets Favors Coalescence, *Phys. Rev. Lett.* 100 (2008) (2).
- [16] Y. Zhang, J.W. van Nieuwkastele, M. Qiang, P.A. Tsai, R.G. Lammertink, Spatial site-patterning of wettability in a microcapillary tube, *ACS Appl. Mater. Interfaces* 8 (17) (2016) 10657–10660.
- [17] L. Shui, A. van den Berg, J.C. Eijkel, Interfacial tension controlled W/O and O/W 2-phase flows in microchannel, *Lab Chip* 9 (6) (2009) 795–801.
- [18] J. Man, Z. Li, J. Li, H. Chen, Phase inversion of slug flow on step surface to form high viscosity droplets in microchannel, *Appl. Phys. Lett.* 110 (18) (2017) 181601.
- [19] Q. Meng, Y. Zhang, J. Li, R.G. Lammertink, H. Chen, P.A. Tsai, Altering emulsion stability with heterogeneous surface wettability, *Sci. Rep.* 6 (2016) 26953.
- [20] H. Fendler Janos, The colloidal domain: where physics, chemistry, biology, and technology meet. By D. Fennell Evans and Hakan Wennerström. VCH Publishers, New York 1994, XXXII, 515 pp., hardcover, \$65.00, DM 980, ISBN 1–56081–525–6, *Adv. Mater.* 8 (3) (1996) 260–260.
- [21] J.W. de Folter, E.M. Hutter, S.I. Castillo, K.E. Klop, A.P. Philipse, W.K. Kegel, Particle shape anisotropy in pickering emulsions: cubes and peanuts, *Langmuir ACS J. Surfaces Colloids* 30 (4) (2014) 955–964.
- [22] C.M. Bates, F.S. Bates, 50th anniversary perspective: block polymers—pure potential, *Macromolecules* 50 (1) (2016) 3–22.
- [23] E. Dickinson, Milk protein interfacial layers and the relationship to emulsion stability and rheology, *Colloids Surf. B. Biointerfaces* 20 (3) (2001) 197–210.
- [24] J. Farauto, F. Bresme, Origin of the short-range, strong repulsive force between ionic surfactant layers, *Phys. Rev. Lett.* 94 (7) (2005) 077802.
- [25] B.P. Binks, Particles as surfactants—similarities and differences, *Curr. Opin. Colloid Interface Sci.* 7 (1) (2002) 21–41.
- [26] P. Alexandridis, T. Alan Hatton, Poly(ethylene oxide) poly(propylene oxide) poly(ethylene oxide) block copolymer surfactants in aqueous solutions and at interfaces: thermodynamics, structure, dynamics, and modeling, *Colloids Surf. A* 96 (1) (1995) 1–46.
- [27] A. Pitto-Barry, N.P.E. Barry, Pluronic® block-copolymers in medicine: from chemical and biological versatility to rationalisation and clinical advances, *Polym. Chem.* 5 (10) (2014) 3291–3297.
- [28] M.Y. Kozlov, N.S. Melik-Nubarov, E.V. Batrakov, A.V. Kabanov, Relationship between pluronic block copolymer structure, critical micellization concentration and partitioning coefficients of low molecular mass solutes, *Macromolecules* 33 (9) (2000) 3305–3313.
- [29] A. Kumar, S. Li, C.M. Cheng, D. Lee, Flow-induced phase inversion of emulsions in tapered microchannels, *Lab Chip* 16 (21) (2016) 4173–4180.
- [30] T. Brugarolas, D.S. Gianola, L. Zhang, G.M. Campbell, J.L. Bassani, G. Feng, D. Lee, Tailoring and understanding the mechanical properties of nanoparticle-shelled bubbles, *ACS Appl. Mater. Interfaces* (2014).
- [31] A.S. Utada, E. Lorenceau, D.R. Link, P.D. Kaplan, H.A. Stone, D.A. Weitz, Monodisperse double emulsions generated from a microcapillary device, *Science* 308 (5721) (2005) 537.
- [32] Y. Gai, J.W. Khor, S.K. Tang, Confinement and viscosity ratio effect on droplet break-up in a concentrated emulsion flowing through a narrow constriction, *Lab Chip* 16 (16) (2016) 3058–3064.
- [33] G. Gotchev, T. Kolarov, K. Khristov, D. Exerowa, Electrostatic and steric interactions in oil-in-water emulsion films from Pluronic surfactants, *Adv. Colloid Interface Sci.* 168 (1–2) (2011) 79–84.
- [34] D. Exerowa, D. Platikanov, Thin liquid films from aqueous solutions of non-ionic polymeric surfactants, *Adv. Colloid Interface Sci.* 147–148 (2009) 74–87.
- [35] Z. Liu, S.T. Chan, H.A. Faizi, R.C. Roberts, H.C. Shum, Droplet-based electrocoalescence for probing threshold disjoining pressure, *Lab Chip* 15 (9) (2015) 2018–2024.
- [36] B. Steinhaus, P.T. Spicer, A.Q. Shen, Droplet size effects on film drainage between droplet and substrate, *Langmuir ACS J. Surfaces Colloids* 22 (12) (2006) 5308–5313.
- [37] S.I. Karakashev, E.D. Manev, Hydrodynamics of thin liquid films: retrospective and perspectives, *Adv. Colloid Interface Sci.* 222 (2015) 398–412.
- [38] E.D. Manev, A.V. Nguyen, Critical thickness of microscopic thin liquid films, *Adv. Colloid Interface Sci.* 114–115 (2005) 133–146.
- [39] S. Cosima, K. Regine von, Disjoining pressure in thin liquid foam and emulsion films—new concepts and perspectives, *J. Phys.: Condens. Matter* 15 (27) (2003) R1197.
- [40] B. Vance, Forces and structure in thin liquid soap films, *J. Phys.: Condens. Matter* 11 (19) (1999) R215.
- [41] H. Chen, E. Dong, J. Li, H.A. Stone, Adhesion of moving droplets in microchannels, *Appl. Phys. Lett.* 103 (13) (2013) 131605.



- [42] R. Sedev, D. Exerowa, DLVO and non-DLVO surface forces in foam films from amphiphilic block copolymers, *Adv. Colloid Interface Sci.* 83 (1) (1999) 111–136.
- [43] O. Manor, T.T. Chau, G.W. Stevens, D.Y. Chan, F. Grieser, R.R. Dagastine, Polymeric stabilized emulsions: steric effects and deformation in soft systems, *Langmuir ACS J. Surfaces Colloids* 28 (10) (2012) 4599–4604.
- [44] B. Neumann, B. Vincent, R. Krustev, H.-J. Müller, Stability of various silicone oil/water emulsion films as a function of surfactant and salt concentration, *Langmuir ACS J. Surfaces Colloids* 20 (11) (2004) 4336–4344.
- [45] K.C. Powell, R. Damitz, A. Chauhan, Relating emulsion stability to interfacial properties for pharmaceutical emulsions stabilized by Pluronic F68 surfactant, *Int. J. Pharm.* 521 (1–2) (2017) 8–18.
- [46] G. Akay, Sustainable ammonia and advanced symbiotic fertilizer production using catalytic multi-reaction-zone reactors with nonthermal plasma and simultaneous reactive separation, *ACS Sustain. Chem. Eng.* 5 (12) (2017) 11588–11606.