Polymer stretch in two-phase microfluidics: Effect of wall wettability

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Polymer stretching in two-phase microfluidics is investigated by dissipative particle dynamics. The flow patterns can be controlled by wall wettability, flowrate ratio between two phases, and Reynolds number (Re). For neutral and partially wettable walls, segmented flows are formed and polymer stretching can be controlled by Re and segment length. At high Re , stratified flows are observed and the extension ratio can be tuned by the flowrate ratio. For nonwettable walls, slug flows are formed and polymer stretching can be controlled by Re and slug length. At high Re or flowrate ratio, annular flows are observed and high extension ratio can be easily attained. © 2012 American Institute of Physics.

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I. INTRODUCTION

Micro/nanofluidic systems deal with the manipulation of fluids in a channel having cross-sectional dimensions on the order of 10 nm to 100 μ m. Compared to large scale systems, the micro/nanofluidic systems possess unique features such as high surface-to-volume ratio, short diffusion distances, and fast heat and mass transfer.^{1–3} Hence, this system has been extensively used in biological processes such as protein analysis, enzyme-catalyzed reaction, or extension of biopolymers. Stretching biopolymers is an important process because it can provide not only genetic information⁴ but also understanding of protein-DNA interactions at the single-molecule level. As the DNA extension scales linearly with the number of base pairs, the site specific interaction of biological enzymes and fluorescent probes is allowed to be measured with high accuracy.^{5,6} Typical methods of stretching biopolymers include applying a force by a tweezers to an object attached to the free end of biopolymers or exerting a force to the biopolymers along its contour length by electric or hydrodynamic flow fields.^{7–9} Those procedures are usually performed in single-phase flow system. Recently, it is further reported that biopolymers can also be stretched in two-phase flow microfluidics.^{10,11} DNA stretching is observed within the aqueous filament undergoing thinning and breakup by oil phase or within a submicron constriction created by a closely fitting slug. While local elongational flow can enhance the stretching, film rupture and DNA trapping can occur in some cases.^{12,13}

Flow in a microfluidic system is usually simple. The viscous effect dominates and thus the low Reynolds number leads to laminar flow. Although hydrodynamic instability and nonlinearity are generally absent in microsystems due to negligible inertial effects, complex pattern formations are reported for two-phase flows in microchannels.^{14,15} In fact, instability can be developed when the boundary between the two immiscible fluids is not static. The competition of viscous force and capillary force can be described by the capillary number (Ca), which is typically small compared to unity in a microchannel. As a result, the interfacial tension plays a crucial role in determining the two-phase flow pattern and fluid/fluid meniscus. In addition, the wettability between fluids and microchannel wall also affects the flow behavior significantly

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and can be expressed in terms of the contact angle θ . Following Young's equation, one has $\cos \theta = (\gamma_{AW} - \gamma_{BW})/\gamma_{AB}$ at equilibrium, where γ_{AW} , γ_{BW} , and γ_{AB} represent the interfacial tensions of liquid A-solid, liquid B-solid, and liquid-liquid, respectively. It is reported that the ordered patterns can be observed when the system is in the completely wetting regime ($\theta \approx 0^\circ$), while disordered patterns are produced in the partially wetting regime ($\theta > 0^\circ$).¹⁵

When two immiscible fluids in the partially wetting regime are introduced into the microchannel at comparable rates, each segment of fluids appears alternately and this kind of flow has been referred to as the biphasic segmented flow or alternating flow. The internal circulation is usually generated within each segment, which is stimulated by the shear between the stationary fluid at the microchannel wall and the segment axis as well as the impenetrability condition between fluid/fluid interface. As a result, the interfacial reaction between adjacent fluid segments of different phases can be facilitated by continuously refreshing interfaces, which is driven by the internal vortex flow.¹⁶ Moreover, such biphasic vortices can be used to manipulate the extension and compression of flowing diblock copolymers. Upon modification of the wall wettability, the flow pattern may be changed and thereby the conformation of flowing polymers is altered as well. In this work, the effect of wall wettability on the flow behavior is investigated by the dissipative particle dynamics (DPD). Further, the stretch of a flowing polymer chain in different steady flow patterns is studied. The method to control the degree of polymer extension is also explored.

II. MODEL AND SIMULATION METHOD

The DPD model explicitly includes water, oil, and polymer, reproduces the correct hydrodynamics¹⁷ and can be used to explore the flow pattern and polymer stretch. The DPD beads represent small fluid volumes rather than single atoms or molecules and thus their interaction potentials become softly repulsive and short ranged.¹⁸ All potentials are taken to have the same range r_c but their amplitudes a_{ij} differ for different bead species. Three species of beads are considered: water (A), oil (B), and tube wall (W) beads. For simplicity, a diblock copolymer consists of a hydrophilic block of N_A A beads and a hydrophobic block of N_B B beads. These polymer beads are connected by harmonic spring potentials with the spring constant k_s ($= 100 k_B T / r_c^2$) and the unstretched length l_s ($= 0.7 r_c$).¹⁹ The microfluidic channel is a cylindrical tube with the radius $R = 10 r_c$. The tube wall is constructed by two layers of static particles and provides a simple bounce back condition to all fluid DPD particles. In DPD simulations, all the units are scaled by the particle mass m , cutoff distance r_c , and thermal energy $k_B T$. Without loss of generality, the interactions among the same beads are assumed the same, $a_{AA} = a_{BB} = 25$ (typical value for normal fluids), but the interaction between the two fluids is set as $a_{AB} = 50$ to ensure immiscibility. In our simulations, there are $N = 293\,294$ beads for tube length $L = 200$. The dimensionless density is $\rho = 4N/\pi R^2 L$ and the chain length is described by $N_A = N_B = 50 \sim 100$. In the absence of polymer, the Hagen-Poiseuille law is obeyed for a single-phase flow and the dimensionless viscosity is therefore determined as $\mu = 0.83$ by obtaining the mean velocity U corresponding to the body force driven flow.

The flow pattern in biphasic microchannels is generally determined by the flowrates of the two fluids and wall wettability. The latter relates to the interfacial tension, which can be evaluated by $\gamma_{ij} = \int_{-\infty}^{\infty} [P_N - P_t(z)] dz$, where the tangential pressure P_N is different from the normal pressure P_t only in the vicinity of the interface.²⁰ In this work, the fluid-fluid interfacial tension is fixed ($\gamma_{AB} \simeq 3.47$) and thereby the wall wettability is tuned by a_{AW} when a_{BW} is specified as 25. In the absence of flow, three scenarios are considered for fluid A : neutral, partially wettable, and nonwetting walls, as demonstrated in Fig. 1. As $a_{AW} = 25$, the contact angle is $\theta = 90^\circ$ because of $\gamma_{AW} = \gamma_{BW} \simeq 5.44$ and train-like segments are formed. When the incompatibility between fluid A and wall is increased to $a_{AW} = 50$, the interfacial tension grows as well, i.e., $\gamma_{AW} \simeq 8.11$. Consequently, the segment of fluid A changes into a convex shaped plug and the static contact angle determined from the simulation is about $\theta = 140^\circ$, which agrees with the calculation based on Young's equation. As the wall wettability is further reduced to $a_{AW} = 100$, the tube wall becomes nonwettable by fluid A and alternating slugs enclosed by a thin layer of fluid B are formed.

FIG. 1. Flow patterns of two-phase microfluidics at different Reynolds numbers in (a) neutral, (b) partially wettable, and (c) nonwettable wall.

III. RESULTS AND DISCUSSION

When the fluid is in motion, the dynamic pressure near the rear meniscus of the segment is higher than that near the front meniscus. As a result, the shape of the segment is altered and furthermore the flow pattern changes for high enough Reynolds number (Re) because the fluid inertia becomes important. Here, $Re = 2\rho UR/\mu$ and $Ca = \mu U/\gamma_{AB}$. For typical two-phase microfluidic systems, $Re \lesssim 40$ and $Ca \ll 1$ and our simulations are within this range. Figure 1 demonstrates the variation of the biphasic flow characteristics with Reynolds number at various wall wettabilities. The steady flow is in a periodic fashion and the volume ratio of the two fluids is 1:1. For neutral and partially wettable walls, the flowing segments deform due to pressure drop along the segment, as depicted in Figs. 1(a) and 1(b). The receding angle is smaller than the static contact angle while the advancing angle is greater than the static contact angle. As Re is further increased, however, the segmented flow turns into the stratified flow, in which each fluid occupies half the tube. On the other hand, the flow of deformed slugs is observed for a nonwettable wall, as shown in Fig. 1(c). The slug is elongated compared with that in the absence of flow. Owing to pressure drop, the front meniscus of the slug becomes sharper while the rear of the slug flattens. The slug flow transforms into the annular flow with fluid A flowing in the core and fluid B flowing on the wall. It is different from the stratified flow, as illustrated from the cross section of the tube. Consequently, four kinds of stable, biphasic flows can be achieved: segmented, stratified, slug, and annular flows.

Just like surfactant molecules prefer residing at the interface, the diblock polymer chain tends to anchor at the fluid-fluid interface due to its amphiphilic nature. Both coil blocks expand in the corresponding good solvents. For the segmented flow, the internal circulations in the neighboring segments create an extensional flow in the vicinity of the interface. As a result, the coil block in the leading segment is stretched while the coil block in the following segment is compressed, as shown in Figs. 2(a) and 2(c) for neutral walls. Note that the polymer chain can be stretched in either fluid A or fluid B. Moreover, the extent of the polymer stretch generally rises as the flowrate is increased. That is, the flowrate enhances the internal circulation and the rate of strain, which in turn facilitate polymer stretching. Similar polymer stretch can be observed in the slug flow. However, the mean velocity of the slug is larger than that of the continuous phase and therefore the polymer chain is always dragged to the rear of the slug. The extension flow taking place at the rear interface extends the coil block within the slug, as illustrated in Fig. 2(b) for nonwettable walls.

The quantitative variation of the polymer extension with the Reynolds number is further shown in Fig. 3 for both segmented and slug flows. The extension $\langle E \rangle$ for the stretched block is defined as

FIG. 2. Snapshots of polymer stretching at different Reynolds numbers in (a) segmented and (b) slug flows. Polymer extension grows with increasing Re . (c) A schematic picture describing the internal circulation in the frame of moving with the slug. For a diblock copolymer pinned at the interface, polymer stretching/compression is caused by the extensional flow along the elongated/contracted direction.

ratio of the mean polymer length along the microchannel to the maximum elongation, which is equal to $(N_A - 1)l_s$. In the regime of segmented flows, polymer stretching grows with increasing Re at small Re . However, when Re is high enough, the polymer extension reaches a maximum and is maintained at this length regardless of the flowrate. Figure 2(a) illustrates that the free end of the stretched polymer is confined at the front meniscus of the segment. This result reveals that the polymer extension can be enhanced by the increment of the strain rate of the extensional flow, but it is also limited by the length of the segment (L_s) which is essentially independent of Re . Similar to the segmented flow, polymer stretching in the regime of slug flow is also increased as Re rises. Nevertheless, the behavior of both regimes is somewhat different. The polymer chain within the slug continues extending even at higher Re . It can be attributed to the increase of the strain rate and the elongation of the slug, although the volume ratio remains at 1:1 in a period of length. That is, the limitation associated with the slug size can be relaxed by the flowrate increase in the slug flow. Since the elongation effect gradually becomes important with increasing Re , the polymer extension also grows accordingly. Apart from stretching the coil block in the leading segment, the extensional flow in the vicinity of the interface compresses the coil block in the trailing segment. The compression for the compressed block can be defined as the ratio of the radius of gyration perpendicular to the flow direction (R_v) to that in the quiescent state (R_{v0}). As illustrated in the inset of Fig. 3, the extent of polymer compression rises and reaches its maximum value as Re is increased. The saturation effect may be due to the partially relaxation of polymer by the highly deformed interface. We

FIG. 3. The variation of the extensional ratio $\langle E \rangle$ with Reynolds number in neutral and nonwetttable walls. The extent of compression for the compressed block is shown in the inset in the segmented flow. R_v denotes the radius of gyration perpendicular to the flow direction and R_{v0} is for a quiescent state.

have also found that the polymer compression is less significant in the slug flow than in the segmented flow.

In addition to the strain rate of the extensional flow, polymer extension can be controlled by the segment size in the segmented flow. The segment size can be tuned by the injection frequency and the ratio of the flowrates of the two fluids, Q_A/Q_B . At given flowrates, the segment length declines with increasing the injection frequency. Figure 4(a) shows the variation of the polymer extension with the segment size for $Q_A/Q_B = 1$ at $Re \approx 5.7$. The approximately linear growth behavior of the polymer extension before reaching its maximum value confirms that the polymer stretch by the extensional flow is confined by the segment length. At a given injection frequency, the polymer extension can also be controlled by the relative flowrates. For approximately the same Re , the segment size of fluid A rises with increasing Q_A/Q_B . Therefore, the polymer extension is

FIG. 4. (a) The variation of the extensional ratio $\langle E \rangle$ with segment length (L_s) in segmented flows for $Q_A/Q_B = 1$ at $Re \approx 5.7$. (b) The variation of the extensional ratio $\langle E \rangle$ with the flowrate ratio Q_A/Q_B for segmented flows at $Re \approx 4.7$.

FIG. 5. Snapshots of polymer extension in a stratified flow with different fluid volume ratios (or Q_A/Q_B) at $Re \simeq 26$.

enhanced at higher Q_A/Q_B , as demonstrated in Fig. 4(b) for $Re \approx 4.7$. However, when the segment length is long enough, the polymer extension is limited by the mean flowrate.

When Re is high enough, the segmented and slug flows are no longer stable. For neutral walls, the stratified flow is formed and polymer extension can be observed as shown in Fig. 5. For the flowrate ratio $Q_A/Q_B = 5.3$ and $Re \simeq 26.0$, the extension ratio reaches $\langle E \rangle = 0.83$. The interface provides an anchored place for both coil blocks and thus they are stretched by the shear flow. Different from polymer stretching in segmented and slug flow, both coil blocks are stretched at the same time. The coil in the phase with higher flowrate is pulled forward while the coil in the phase with lower flowrate is extended backward. At approximately the same Re , the extension ratio declines as Q_A/Q_B decreases. For $Q_A/Q_B = 1$, the ratio reduces to $\langle E \rangle = 0.32$ and backward stretching of both coils is preferred. For nonwetttable walls, the annular flow can be seen for $Q_A/Q_B = 1$ at high Re or for high Q_A/Q_B even at low Re . Polymer stretching is clearly observed because of polymer anchored at the interface and the mean velocity difference between the two phases. The mean velocity of the core domain is higher than that of the annular domain formed by fluid B . Figure 6 shows the variation of the extension ratio with Re for the fluid volume ratio 4:1 ($Q_A/Q_B \simeq 14.9$). Evidently, the extension ratio grows

FIG. 6. The variation of the extension ratio $\langle E \rangle$ with Reynolds number in an annular flow for the fluid volume ratio 4:1 ($Q_A/Q_B = 14.9$).

with increasing Re and it can reach $\langle E \rangle \simeq 0.85$ at $Re = 15$. This consequence reveals that the annular flow in a microchannel is an effective approach to control polymer stretching.

In order to make a comparison between simulation and experiment, we choose $r_c = 10$ nm and $m = 8.3 \times 10^{-21}$ kg estimated from benzene with radius 0.25 nm. The channel diameter is 200 nm and the mean velocity for $Re = 5.7$ is 5.4 cm/sec. For $N_A = N_B = 100$, the chain length is about 690 nm. Although our nanofluidic system is small compared to typical microfluidic devices, our simulation results can be applied to larger system based on the scale-up principle.²¹ Suppose we want to build an experimental system, in which exactly the same flow patterns occurs as our simulation system. The two systems need to have geometric and dynamic similarity in terms of dimensionless groups. Since $\langle E \rangle = f(L_s/R, Re, Ca, Q_A/Q_B)$, the geometric similarity is satisfied for the same L_s/D and the dynamic similarity is achieved at the same Re , Ca , and Q_A/Q_B . As a result, the parameters in simulations can be transformed into actual conditions in experiments. Surfactant addition is commonly done to avoid clogging problem.²² The effect of surfactant addition has been simulated. The leading behavior of polymer stretch does not change because the extensional flow due to internal circulation still exists. However, the presence of surfactant can influence the wall wettability and in turn the flow pattern. Thereby, the polymer extension ratio is altered as well.

IV. CONCLUSIONS

Sheared polymers have a tendency to align in the direction of the shear flow and partially stretching of individual polymers in the flow direction is caused by viscous drag acting on the chain, which has been invoked to explain shear-thinning behavior in dilute polymer solutions. Nonetheless, polymer extension by single-phase flow in a microchannel is about 16% even when Re is as high as 16.²³ In this work, we demonstrate that two-phase microfluidics can be employed to stretch diblock copolymers in a systematical manner. The flow patterns can be controlled by wall wettability, flowrate ratio, and Reynolds number. For neutral and slightly wettable walls, the segmented flow is formed and polymer stretching can be controlled by Re and segment length. At high enough Re , the stratified flow is observed and the extension ratio can be tuned by relative flowrates. For nonwetable walls, the slug flow is formed and polymer stretching can be controlled by Re and slug length. At high enough Re or Q_A/Q_B , the annular flow is observed and high extension ratio can be achieved easily.

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