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

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An easy assembling-disassembling co-axial capillaries microfluidic device was built up for the production of double droplets. Uniform polymer core-polymer shell particles were synthesized by polymerizing the two immiscible monomer phases composing the double droplet. Thus poly(acrylamide) core-poly(tripropylenglycol-diacrylate) shell particles with controlled core diameter and shell thickness were simply obtained by adjusting operating parameters. An empirical law was extracted from experiments to predict core and shell sizes. Additionally uniform and predictable non-spherical polymer objects were also prepared without adding shape-formation procedures in the experimental device. An empirical equation for describing the lengths of rod-like polymer particles is also presented.

1 Introduction

How to predict and control the colloidal particle morphology to achieve desirable physical properties has been a major subject over the past few decades [1]. Especially there is growing interest in the synthesis of core-shell particles and non-spherical particles for their potential applications in drug-delivery, immobilization templates and so forth [2-3]. Various techniques for preparing these particles have been reported. Generally core-shell polymer particles are synthesized by a two-stage emulsion polymerization process [4-6]. Other methods include the seeded dispersion polymerization process [7], emulsion polymerization using reactive or polymeric surfactants [8-9] and self-assembly of charged polymers [10-11]. All these polymerization techniques are not only multistage processes but also result in a highly broad particle size distribution which limits some emerging applications such as designer pharmaceuticals and optical display technologies [12-13].

A new route to the fabrication of uniform emulsions is suggested by microfluidic techniques [14-16]. Using this approach, uniform polymer particles [17-18], including Janus spheres [19], discoids [20] and liquid core-polymer shell particles [33] have been prepared. Usually a PDMS microfluidic device is used to fabricate double emulsion hardened through UV- or thermally-induced polymerization into solid core-shell particles [22]. But this process requires highly complex and difficult spatial control of the surface energy of the PDMS channels to avoid phase inversions [23]. Recently capillary-based microfluidic devices were used for the production of single and liquid-monomer multiple-core droplets [24-26]. The main advantage of these devices is the relative easiness to keep the dispersed phase away from the wall of the device which prevents any phase inversion. Thus

double emulsions can be produced.

In this paper a flexible two co-axial capillaries microfluidic device was designed and used for synthesizing monodisperse polymer core-polymer shell particles. This device consists of inexpensive and commercially available capillaries, ordinary laboratory tubing, syringe pumps, syringes, which might pave the way for applying this system to an industrial production. Following this approach, highly monodisperse double droplets and polymer core-polymer shell particles can be easily obtained. The shell's thickness, core's diameter and the number of cores per particle can be precisely controlled. Additionally monodisperse and size-controlled anisotropic polymer particles, that are usually prepared by an additional deforming procedure, can be conveniently obtained by adjusting the two capillaries' tips relative position.

2 Experimental section

Co-axial capillaries microfluidic device

The device was composed of capillaries with hydrophilic (Fused silica tubing, Polymicro Technologies) or hydrophobic (PEEK or PTFE tubings, Upchurch Scientific) inner walls, T-junctions (P-728-01, Upchurch Scientific), gas-tight syringes, syringe pumps (PHD 2000, Harvard Apparatus), UV light (Lightningcure LC8, Hamamatsu) and tubing (Polytertrafluoroethylene, Fisher Scientific Bioblock).

As shown in Fig. 1, two co-axial capillaries were inserted inside a T-junction along its main axis. Three different devices were obtained depending on the two capillaries' tips relative position (Δ). The inner capillary tip exited at the same position that the middle capillary tip ($\Delta = 0$, cf. Fig. 1.A) or either further downstream ($\Delta > 0$, cf. Fig. 1.B) or upstream ($\Delta < 0$, cf. Fig. 1.C). Three syringe pumps were used to deliver the outer, middle and inner phases at a specific and constant flow rate. To get a double emulsion, inner and middle

solutions were immiscible fluids (two different monomer solutions) as well as the middle and outer phases. By varying the inner and outer diameter of the two capillaries 6 different systems were tested as shown in Table ESI.1.

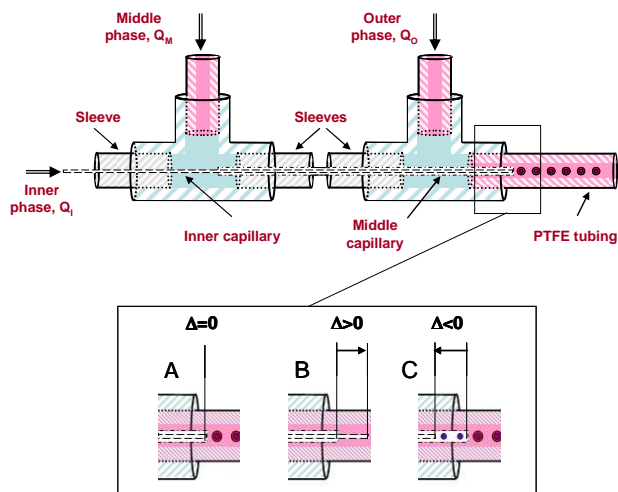


Fig. 1 Schematic drawing of the different co-axial capillaries microfluidic devices used for the production of polymer core-polymer shell particles:

(A) device with the same capillaries' tips relative position ($\Delta = 0$); (B) device with a positive capillaries' tips relative position ($\Delta > 0$); (C) device with a negative capillaries' tips relative position ($\Delta < 0$).

Materials

An aqueous solution of methyl cellulose (Alfa Aesar) in distilled water was used as the continuous phase (outer fluid). The viscosity varied with the amount of methyl cellulose from 500 to 2000 cP. The middle fluid consisted of tripropylenglycol-diacrylate (TPGDA) (Aldrich), 93 wt %; Span80, 3.5% and 1-hydroxycyclohexyl phenyl ketone (HCPK) as a photoinitiator (Aldrich), 3.5 wt %. The inner fluid was composed of acrylamide (AA) (Aldrich), 10 wt %; NN'-methylene-bisacrylamide (ACROS) as a crosslinker, 1.5 wt % and ammonium persulfate (APS) as a thermal initiator (Aldrich), 0.15 wt %.

Polymerization and characterization

The monomer solution composing the main droplet was polymerized through UV irradiation by means of an UV source operating at $\lambda = 365$ nm which corresponds to the maximum of absorbance of the photoinitiator added to the middle phase. The core of the core-shell polymer particles was polymerized by thermal initiated polymerization at 50°C for 120 minutes. Direct observation of the droplet formation was made by coupling a CCD camera (Pike F-032B, Allied Technology) with a microscope (Eclipse 80i, Nikon). The camera captures up to 200 fps at a full resolution of 648 x 488 pixels.

The overall diameter, core diameter and shell thickness of the particles and droplets were measured using the image analysis module of the software controlling the CCD camera (Hiris, R&D vision). The polymerized particles were collected at the exit of the outlet PTFE tubing. Average diameter, d , and standard deviation of the particle diameter distribution, σ , were thus determined by measuring the diameter of at least 50

polymer particles.

The viscosity of the monomer solutions was measured with a Ubbelohde capillary viscosimeter (type 531 10 I, Schott-Geräte). The viscosity of the outer phase was measured with a rheometer (Rheo RV8, spindle 6, 50 rpm).

3 Results and discussions

Device with the same capillaries' tips relative position ($\Delta = 0$)

As shown in Fig. 2a,c the microfluidic devices were designed with the same capillaries' tips relative position. The inner capillary was used to generate core droplet and the middle capillary was used to produce shell layer. These core-shell or droplet-in-drop structures were dispersed in an outer continuous aqueous solution of methyl cellulose. The difficulties of modifying the surface energy of microchannel-based devices to form double droplets was conveniently overcome by using capillaries with hydrophilic/hydrophobic inner walls. Using these microfluidic devices, uniform polymer core-polymer shell particles (CV below 3%) with polyamide core and polyacrylate shell were synthesized as show in Fig. 2.b,d. Core and shell sizes can be precisely controlled by adjusting the capillary geometry, the fluids' flow rates and fluids' viscosities.

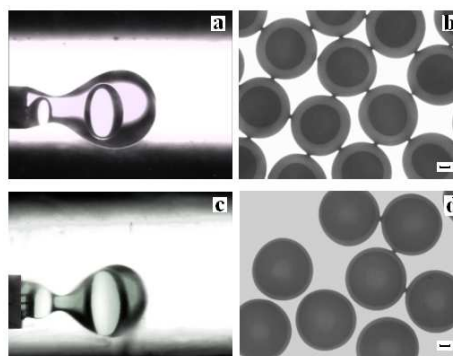


Fig. 2 Snapshots of the formation of the double droplets at the exit of the two co-axial capillaries of system 1 for $\Delta = 0$ (a,c); optical microscopy images of poly(acrylamide) core-poly(tripropylenglycol-diacrylate) shell particles with different shell thicknesses (b,d), core being labeled with an aqueous dye (Nigrosin, Aldrich). Scale bar is 100 μm ; coefficient of variation for the core size distribution is 2.81% (top) and 2.51% (bottom); coefficient of variation for the particle size distribution is 1.52% (top) and 2.12% (bottom). Operating conditions are to be found in the Electronic Supplementary Information.

It is known that the droplet formation from two continuous co-flowing liquids is achieved either in dripping or jetting mode [21]. The continuous and dispersed phase flow rates are key parameters for mastering droplet formation mode. If the dispersed phase flow rate is such that $Q_d < \pi(d^3\gamma/2\rho d)^{1/2}$ (γ is the surface tension between the continuous and dispersed phase, d the droplet diameter and ρ_d the density of the dispersed fluid) the dripping droplet formation will occur [24]. In our experiments we worked at relatively low velocity of all fluids, and the droplets are formed in the dripping mode which ensures formation of highly monodisperse double droplets.

Core size. For co-axial capillary-based microfluidic devices, the drop formation involves a balance between the interfacial tension and the viscous drag imposed by the flow of the

surrounding fluid. Fig. 3b,c shows that while keeping other parameters fixed, the core droplet diameter (d_{core}) decreases while increasing the flow rate of the middle and outer phase fluids owing to the larger shear stress exerted by the surrounding flowing fluids. However this decrease is not

linear and the d_{core} decrease rate becomes smaller as the flow rate of the middle and outer phase fluids increases. Note that a further increase in Q_{O} or Q_{M} generates droplets without any core.

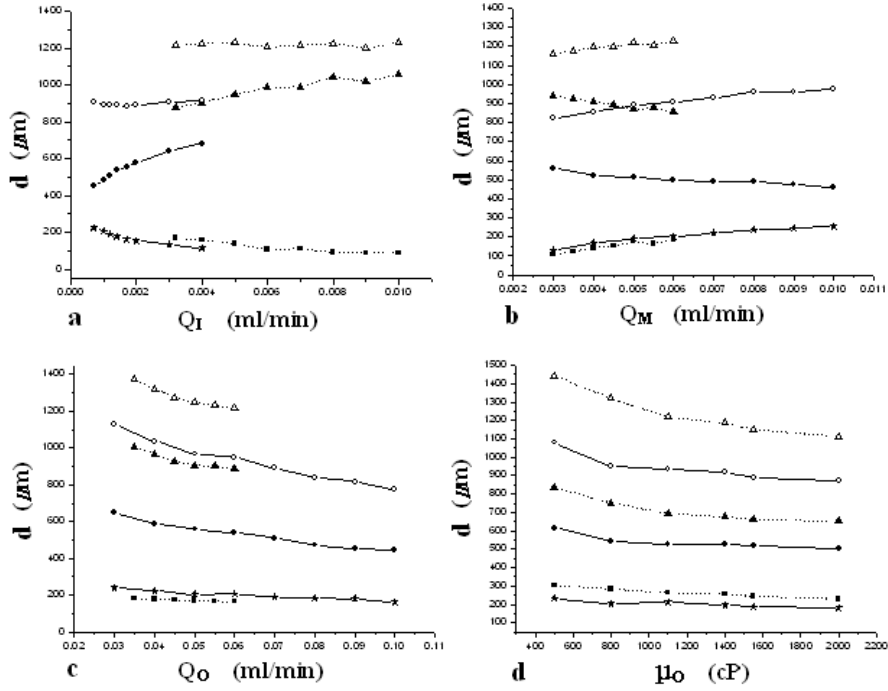


Fig. 3 Influence of fluids' flow rates and outer continuous fluid viscosity on the core and overall droplet size as well as on the shell thickness of the core-shell droplets: (a) effect of the inner fluid flow rate; (b) effect of the middle fluid flow rate; (c) effect of the outer fluid flow rate; (d) effects of outer fluid viscosity. ● core droplet diameter d_{core} , ○ overall droplet diameter d_{drop} , ★ shell thickness d_{shell} , obtained in microfluidic device I; ▲ core droplet diameter d_{core} , Δ overall droplet diameter d_{drop} , ■ shell thickness d_{shell} , obtained in microfluidic device II. Operating conditions and standard errors (Table ESI.2) are to be found in the Electronic Supplementary Information

Under keeping $Q_{\text{O}}/Q_{\text{M}}$ constant, the effects of outer and middle phase fluids' flow rates on the core size are in agreement with the results obtained in single axial capillary microfluidic systems [25], i.e. the core droplet diameter decreases while increasing the outer phase fluid flow rate (cf. Fig. ESI.1).

Besides fluid flow rate, the fluid viscosity also strongly affects the droplet formation. From Fig. 3d, one can find that the higher the viscosity of the outer phase fluid, the smaller is the core droplet diameter. This is due to the increase in the shear force exerted on the middle phase which induces a shorter breakup time of the core-shell droplet.

An interesting consideration is to predict the core droplet size. In all systems tested, it was observed that the core and the overall core-shell drop had the same formation time, i.e. $t_{\text{breakup, core}} = t_{\text{breakup, overall drop}}$. According to $t_{\text{breakup, core}} = V_{\text{core}}/Q_{\text{I}}$ and $t_{\text{breakup, overall drop}} = V_{\text{drop}}/(Q_{\text{I}} + Q_{\text{M}})$, (V_{core} and V_{drop} are the volume of the core and overall drop respectively) one got a relation between the core diameter and the overall drop diameter (equation 1). All experimental data were fairly well described by this relation (cf. Fig. ESI.2).

$$d_{\text{core}} = \sqrt[3]{\frac{Q_{\text{I}}}{Q_{\text{I}} + Q_{\text{M}}}} d_{\text{drop}} \quad (1)$$

Overall droplet size. There was always some interest to predict the overall diameter (d_{drop}) of single and multiple droplets in microchannel- and capillary-based microfluidic devices [24, 27-30]. In a previous work we have described an empirical relation which fairly predicts the average particle diameter obtained from a single capillary microfluidic device [28]. Applying the same methodology to the formation of double droplets, we found (cf. Fig. 4) that the same kind of relation holds between the normalized overall droplet diameter ($d_{\text{drop}}/d_{\text{I}}$, middle cap) and the ratio between the capillary numbers of the outer and middle phase fluids ($\text{Ca}_{\text{O}}/\text{Ca}_{\text{M}}$). It was also found that the overall droplet diameter was not influenced by the inner fluid as it remained constant while increasing the inner fluid flow rate. It is ascribed to the shear stress at the outer/middle interface which remains almost invariant when changing the inner fluid flow rate. Thus the core-shell drop diameter can be predicted by equation 2.

$$\frac{d_{drop}}{d_{I,middle\ cap}} = K \left(\frac{Ca_O}{Ca_M} \right)^{-0.22} \quad (2)$$

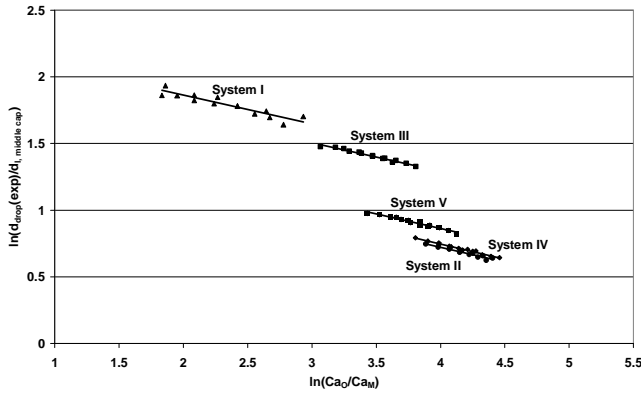


Fig. 4 Variations of the normalized overall droplet diameter as a function of the ratio between the capillary numbers of the outer and middle phase fluids.

Shell size. As for the core and overall droplet diameters, the shell thickness can be changed by adjusting the operating conditions. Fig. 3a,c,d indicate that the shell thickness decreases almost linearly with an increase of inner or outer phase flow rate and outer fluid viscosity. Oppositely, the shell thickness increases by increasing the middle phase flow rate (Q_M) as shown in Fig. 3b. These variations are derived directly from the variations of the core and overall droplet diameters as the shell thickness (d_{shell}) can be calculated by the following equation: $d_{shell} = (d_{drop} - d_{core})/2$. Recalling equation 1, the shell thickness is then given by equation 3.

$$d_{shell} = \frac{1}{2} \left(1 - \sqrt[3]{\frac{Q_I}{Q_I + Q_M}} \right) d_{drop} \quad (3)$$

where Q_I , Q_M , Q_O are the inner, middle and outer fluids' flow rates respectively.

From the above results the procedure to tune the double droplet size (e.g. overall and core diameters, shell thickness) is to set at first the outer and middle fluids' flow rates to get the desired overall droplet diameter. Then by adjusting the inner fluid flow rate, one can target a specific core diameter or shell thickness. This is made possible because the inner fluid flow rate has no influence on the overall droplet diameter as discussed earlier.

Device with a positive capillaries' tips relative position ($\Delta > 0$)

The co-axial capillaries geometry is also a factor which influences the preparation of core-shell particles. In such microfluidic device, the capillaries' tips relative position can easily be adjusted. When the inner capillary tip was moved downstream relatively to the middle capillary tip (cf. Fig. 1B) larger double droplets were formed (cf. Fig. ESI.3A-A', B-B', C-C'). However there was no much effect on the core droplet diameter (cf. Fig. ESI.3). It is attributed to the position of the drop pinch-off which moved downstream as Δ was increased resulting in an increase in the core formation time. Note that

when the distance between the inner and middle capillary tips was beyond the drop breakup length, single droplets of middle fluid were obtained as the inner phase was directly delivered into the outer fluid phase (cf. Fig. ESI.3D-D').

Device with a negative capillaries' tips relative position ($\Delta < 0$)

When the inner capillary tip was moved upstream relatively to the middle capillary tip (cf. Fig. 1C), droplets with smaller and multiple cores were produced. Thus this simple co-axial capillaries microfluidic device had fully the same functions as other sequential microfluidic devices [25-26]. The core droplet diameter, the number of core per droplet and finally the overall droplet diameter can be conveniently adjusted by changing the dimensions of the inner and outer capillary as well as the three fluids' flow rates. As an example several core-shell droplets and their subsequent polymer core-polymer shell particles having different number of cores are presented in Fig. ESI.4. The relation among the number of cores, core and droplet diameter, inner and middle fluid flow rates abides by $N = (d_{drop}/d_{core})^3 / (1 + n)$, where N is the number of cores, n is the ratio of Q_M to Q_I , which is consistent with previous observations in two sequential co-flow microfluidic devices reported by Chu *et al.* [25].

The wetting properties of the capillaries' inner and outer surfaces determine the type of dispersion that can be prepared. Co-axial capillaries microfluidic devices with hydrophobic outer surface of the inner capillary or hydrophobic inner surface of the middle capillary were used so far to generate hydrophilic core-hydrophobic shell polymer particles. By using the same capillary material (e.g. fused silica) for the inner and middle capillary along with a negative capillaries' tips relative position, rod-like polymer particles were synthesized (cf. Fig. 5c) without any additional shape-deforming process that it is usually necessary to prepare non-spherical polymer [26, 31]. The fluid of inner capillary was distilled water while the middle fluid was composed of a hydrophobic monomer solution (TPGDA).

The diameter of the rod-like polymer particle is thus determined by the inner diameter of the middle capillary. Its length (L) can be controlled by adjusting the inner and middle fluids flow rates. The length of these anisotropic particles decreases or increases when the inner and middle fluid flow rates are increased respectively (cf. Fig. ESI.5). For the smallest middle phase flow rate reachable by the pump ($0.0001 \text{ mL}\cdot\text{min}^{-1}$), the length was found equal to a constant value $b = 323 \text{ }\mu\text{m}$. From Fig. 5a it is seen that the monomer droplets was no longer formed in the dripping regime. The droplet formation images strongly suggest a blocking-pinching mechanism as described by Guillot and Colin [32] for cross-flow microchannel-based systems. In this mechanism, the droplet formation is not anymore controlled by the competition between the interfacial tension and the viscous force but rather by the wetting properties of the liquids with regards to the middle capillary inner wall. As the water (inner phase) wets preferentially the glass, a meniscus of water grows from the inner capillary tip till filling entirely the inner diameter of the middle capillary, therefore blocking the flow of middle phase (monomer). For extremely low flow

rates, the middle phase flow can not get through the water meniscus and no monomer droplet is observed. As the flow rate increases, the flow of monomer phase starts to pinch the water meniscus (cf. Fig. 5a) and eventually release a water droplet. Then a new water meniscus grows, blocks the monomer phase and so forth. Thus one can observe droplets of water wetting the middle capillary inner wall and plugs of monomer phase (cf. Fig. 5c).

By plotting on a logarithmic graph the variations of L versus Q_M/Q_I , a straight line was obtained (cf. Fig. ESI.6). So an empirical law describing the relations between the length of the rod-like particles and fluid flow rates was extracted (Equation 4) allowing to quantitatively predict the designated rod-like polymer length. Note that this equation is only valid when the middle phase flow rate is greater than $0.0001 \text{ mL}\cdot\text{min}^{-1}$; due to the pump limitations, it was not possible to investigate lower flow rates. However we have verified that no droplets were formed when the middle phase flow rate is set to zero.

$$L = b + 85.62 \left(\frac{Q_M}{Q_I} \right)^{1.92} \quad (4)$$

where b is equal to 323 in this experiment.

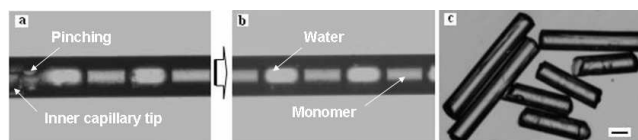


Fig.5 Snapshots of the formation of non-spherical drops (a,b) and the optical microscopy images of the subsequent rod-like poly(TPGDA) particles obtained by varying the ratio of the middle to inner fluid flow rates (c) in microfluidic system VI. Scale bar is $200\mu\text{m}$. Operating conditions are to be found in the Electronic Supplementary Information

4 Conclusions

We have designed a two co-axial capillaries microfluidic device for the production of highly uniform double droplets which were polymerized downstream to produce polymer core-polymer shell particles. The device was easily assembled from cheap commercially available parts. Thus uniform poly(acrylamide) core-poly(tripropylenglycol-diacrylate) shell particles were synthesized in this flexible microfluidic device. Based on empirical laws, we propose a procedure for adjusting independently the overall particle and core diameters. Depending on the relative position of the inner and middle capillaries' tips, particles with one or more cores were obtained. Uniform anisotropic polymer particles were also prepared with this flexible microfluidic device without any deforming procedures. The particle geometrical properties can be precisely controlled by adjusting the fluids' flow rates and continuous phase viscosity. New empirical laws for predicting core-shell and rod-like polymer particles size are given.

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