

Millifluidic as a versatile reactor to tune size and aspect ratio of large polymerized objects

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Abstract

The continuous production “on demand” of large polymerized objects is presented using a versatile, easy to implement and low cost “millifluidic” reactor. Over microfluidic devices, the present set-up offers two considerable advantages: (i) much larger particles are produced with a very good control of sizes and shapes and (ii) no lithography is required for its design. Considering the high modularity of this synthetic pathway, “tubular millifluidic” appears as a new concept of synthesizing particles with a strong control over final object sizes, monodispersity and aspect ratio. The possibility to reach a high scale production makes it a promising production tools for the industry.

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1. Introduction

There is today a strong and emerging interest toward designing novel and complex architectures which can respond to society’s particular needs in advanced technology or in the medical field. In this general context, as recently postulated by Backov (2006), chemistry, physical-chemistry, physics and biology can be assembled within a new concept of “integrative chemistry” that appears as a versatile tool-box dedicated to design and create novel hierarchical architectures. Along this line, hierarchically organized structures patterns can be used at different length scales. For instance, Imhof and Pine (1997), Binks (2002) and Carn et al. (2004) make the use of lyotropic mesophases at the mesoscale while employing bi-liquid foams as macroscopic templates. Similarly, air-liquid foams macroscopic templates can be used to shape either silica as demonstrated by Carn et al. (2004), titanium dioxide proposed by Carn et al. (2005) or vanadium oxide shown more recently by Carn et al. (2005). As shown by Biette et al. (2005) and Serier et al. (2006), previous thermodynamically metastable systems can also be substituted by the appliance of external fields, as it is the case for the extrusion

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process where a shear rate is applied to a syringe out-coming vanadium oxide sol droplets. Along these lines, the recent advances of continuous flow microfluidic synthesis offer a new pathway to tailor complex colloidal systems. An important advantage of this method over batch polymerization, as noticed by Anna et al. (2003), is the possibility to produce narrow size particle polydispersity (below 2%). In the last two years, Seo et al. (2005), Pollauf et al. (2005), Lewis et al. (2005), Sugiura et al. (2001, 2002) or De Geest et al. (2005), have reported the rapid continuous synthesis of monodisperse particles using microfluidic continuous flow reactors. More recently, Nie et al. (2005) and Dendukuri et al. (2005) have even shown that the control of the geometrical constraints of these reactors can be used to generate non-spherical particles with a very good control over their aspect ratio and size. As noted by Brivio et al. (2006), the high heat and mass transfer rates provided by the microfluidic reactors offer safe and rapid synthesis. Such a feature may permit to explore and develop new chemical pathways impossible to achieve with batch reactors.

Herein, we describe “tubular millifluidic”, a new continuous flow method, to produce polymer particles with a good control of sizes and aspect ratios. The high potentialities of this approach stem from the possibility to generate highly monodisperse liquid reactors and to manipulate and functionalize each one individually “on line”. It leads to extremely narrow size particle polydispersities since no stabilization over coalescence is needed as collisions between droplets are suppressed.

Our “tubular millifluidic” devices are made of glass capillaries (with typical diameters of the order of one millimetre and whose internal morphologies, i.e. sizes and forms can be changed) assembled to each other by means of home made Plexiglas connexions.

The particle sizes produced with millifluidic devices are much larger than those obtained with the PDMS based “microfluidic” devices, i.e. 100 μm up to 3 mm for the former and 20 up to 200 μm for the later. Moreover, due to the larger values of the flow rates involved (typically a few ml/min), reaching a scalable production should be possible by integrating several reactors on a single platform. The production of particles with sizes ranging from 100 μm to few millimetres is important in many fields, as for instance, heterogeneous catalysis, ion exchanges, granular flow and so forth. In many of these applications, the particle sizes, the associated degree of monodispersity as well the aspect ratio appear as important characteristics to be tuned with a certain degree of rational design while employing, as far as possible, a continuous and low cost methodology. For these reasons, we believe that the use of “tubular millifluidic” is not only a promising strategy for the production of large size particles, but also a potential production tool for industry.

Technically, “Tubular millifluidic” droplet based devices present numerous advantages for chemical engineering and processing. These devices do not require any soft lithography or laser etching techniques for their fabrication. Carrying on these technologies is time consuming and requests a financial investment which restricts the emergence and use of the microfluidic techniques in most laboratories and industrial and development research centres. Our “millifluidic” devices are also modular since they can be easily assembled and disassembled. Modifying a device therefore does not require starting at the lithography process. As a result, polymer particle synthesis using these devices, can be implanted in any industrial laboratory or research centre at very low cost and rapidly.

2. Experimental arrangements

NOA (Norland Optical Adhesive) 80, a monomer allowing photo-induced polymerization, and silicone oil were respectively obtained from Epotecny (France) and Fluka. The Gauge of the needle used for the formation of droplets is 16G. The inner diameters of the two capillary glass tubes are, respectively, $D = 2.8$ and $d = 1.3$ mm. The droplet rate of production is measured with a laser diode whose maximum Output and wavelength are, respectively, <1 mW and $\lambda = 630$ nm, illuminating a photodiode connected to a digital oscilloscope. The power density of the UV light source used for polymerization is 130 mW cm^2 .

3. Results and discussion

Fig. 1a shows the design of the millifluidic flow reactor used in the present work previously used by Engl et al. (2005). Briefly, a syringe needle (diameter ranging from 100 μm up to 1.5 mm) is centred in cylindrical glass tube whose inner diameter, D , is 2.8 mm. Using two digitally syringe pumps, the monomer and silicon oil

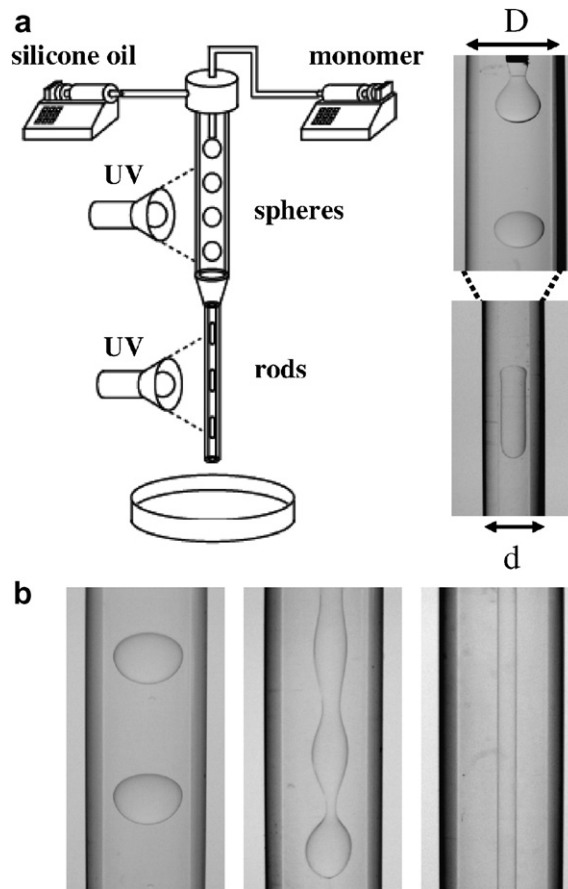


Fig. 1. (a) Millifluidic geometry used to create spherical or rod-like particles fabricated by exposing monomer droplets to UV. (b) Shown are the two different modes of droplet formation (left image) dripping and (central image) jetting and the stable cylindrical stream pattern (right image) observed when droplets do not form.

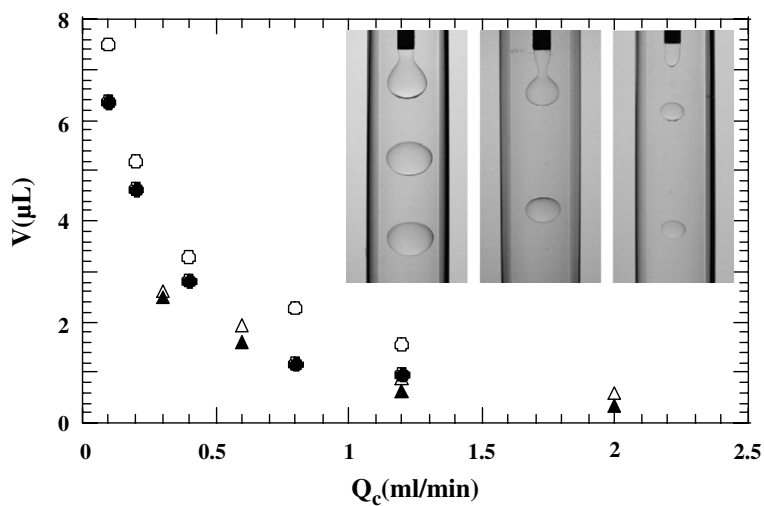


Fig. 2. Sizes of droplets (open symbols) and corresponding particles (closed symbols) obtained after polymerization as a function of Q_c for $Q_d = 0.05 \text{ ml min}^{-1}$ (circles) and $Q_d = 0.02 \text{ ml min}^{-1}$ (triangles). The diameters of the central needle and of the capillary channel are, respectively, 0.8 mm and 2.8 mm.

are, respectively, infused through and around the central needle, as depicted in Fig. 1a. The flow rates of these two immiscible fluids are independently controlled and adjusted in order to form monomer droplets in silicon oil. To avoid any problem due to density mismatch between the droplet and the continuous phase, the glass tube must be placed vertically. As shown in Fig. 1b, two different drop break-up mechanisms can be witnessed. The droplets can either form in the vicinity of the needle tip (dripping regime) or break-up from a cylindrical extended filament due to Rayleigh instability (jetting regime), behaviours already mentioned by Zhang and Stone (1997) or Cramer et al. (2004). The transition between these two regimes depends on Q_c and Q_d , the respective flow rate of the continuous and dispersed phase, η_c and η_d the respective viscosities of these two fluids, γ their surface tension as well as the geometrical parameters characterizing the set-up, namely the diameter of the needle and the inner diameter of the capillary tube and eventually on the Bond number (ratio of the gravity over surface tension effects). It is not the aim of our paper to expand into the details of the physics of

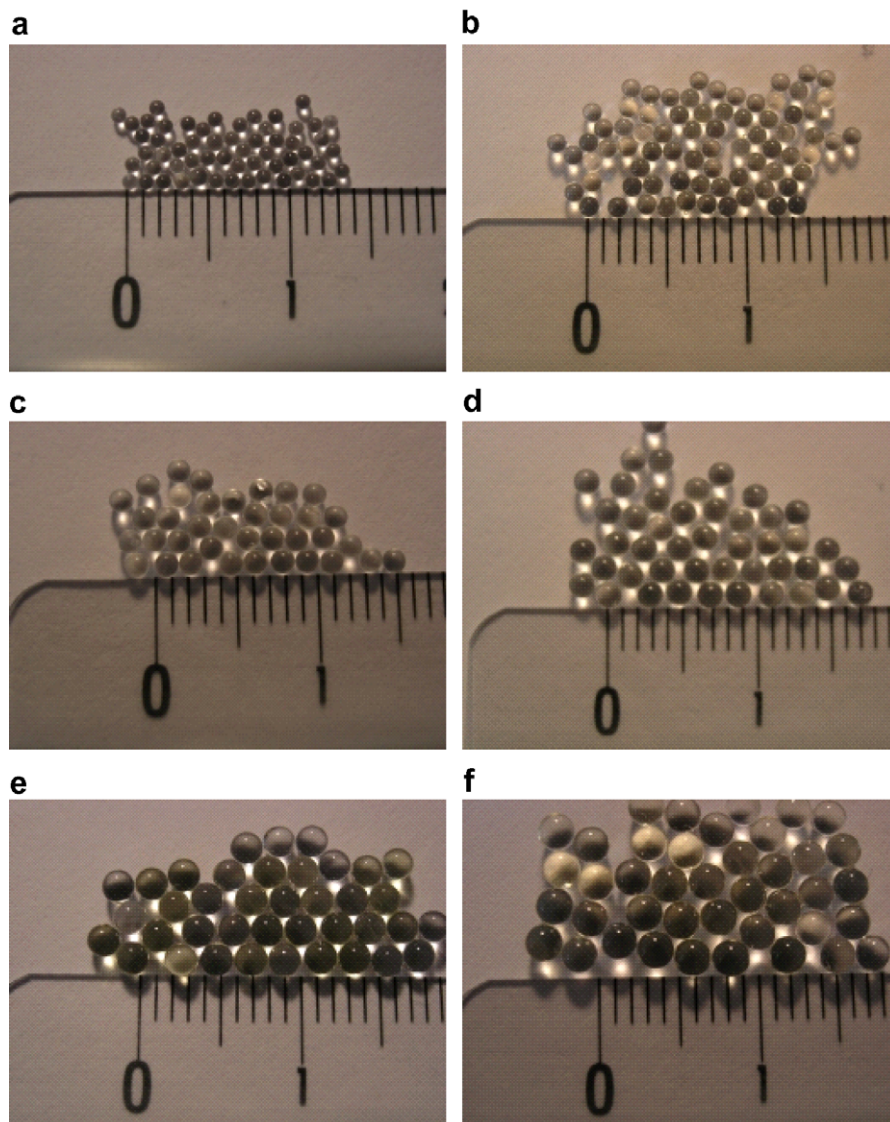


Fig. 3. Spherical particles fabricated after exposing monomer droplets to UV radiation. The flow rates given in ml min^{-1} are: (a) $Q_c = 2$, $Q_d = 0.02$, (b) $Q_c = 1.2$, $Q_d = 0.05$, (c) $Q_c = 0.8$, $Q_d = 0.05$, (d) $Q_c = 0.4$, $Q_d = 0.05$, (e) $Q_c = 0.2$, $Q_d = 0.05$ and (f) $Q_c = 0.1$, $Q_d = 0.05$. The set-up parameters are identical to those of Fig. 2.

dripping and jetting with this set-up. In the dripping mode, the droplets size mainly results from a balance between the capillary and the viscous stress due to the external flow field. In this regime, considering the work from Lewis et al. (2005), the droplets which form at the tip of the needle are very monodisperse in size (the width of their size distribution is less than 2%). When the two immiscible fluids are Newtonian, no satellite droplets are witnessed. Besides, the droplets are emitted at a constant rate, f ; so that in this regime, the tube is filled with a periodic train of droplets. Consequently, by measuring this rate using a Helium Neon laser diode illuminating a photodiode connected to a digital oscilloscope, the droplet volume V can therefore be obtained very simply using the conservation of mass of the disperse phase, namely, $V = Q_d/f$. As shown in Fig. 2, the droplet size strongly depends on Q_d and Q_c and therefore can be conveniently controlled by merely varying these two parameters. Moreover, it can considerably be reduced by taking a central needle with a smaller diameter, or increasing the viscosity of the continuous phase. The monomer droplets are then exposed downstream the vertical glass tube to UV irradiation. As evident in Fig. 3, the obtained particle size is comparable to the droplet size prior to photo-polymerization. Note that its size distribution remains very narrow and seems not tremendously affected by the reaction.

Many applications of polymer particles are governed by their shape in morphologies. By contrast to batch polymerization of homopolymers which leads to the production of spherical particles, “on line” polymerization in the microfluidic device allows for the preparation of particles with non-spherical shapes, as proved by Dendukuri et al. (2005). The principle is very simple since it only takes advantage of the constrained geometry of the device. First monodisperse droplets are generated in the capillary tube of diameter, D . By varying Q_d and Q_c , their volume can easily be controlled (Fig. 4). The shape of the droplets is then determined by the relationship between the diameter of an undeformed droplet given roughly by $r = (3V/4\pi)^{1/3}$ and D . For $r > D/2$, the droplets must adopt a rod shape since the confinement suppresses the relaxation of their shape to the spherical equilibrium one. Consequently, by taking advantage of the confinement, the aspect ratio of these rod-like droplets can be conveniently controlled by merely changing the ratio between the droplet

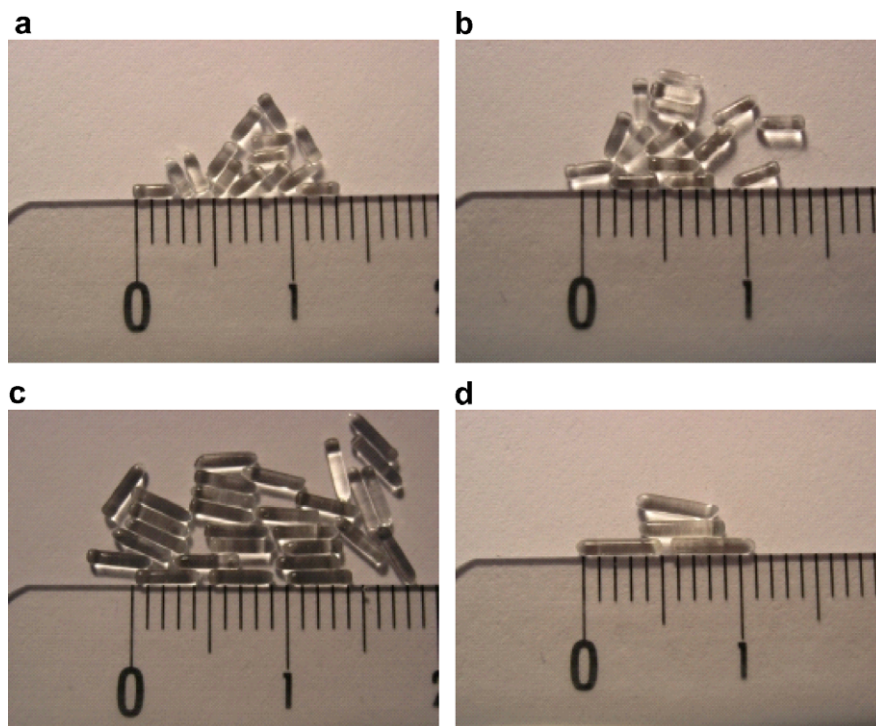


Fig. 4. Rod-like particles obtained after polymerization of the previous droplets in a narrow tube. (a) $Q_c = 0.6$, $Q_d = 0.02$, (b) $Q_c = 0.5$, $Q_d = 0.05$, (c) $Q_c = 0.4$, $Q_d = 0.05$, (d) $Q_c = 0.2$, $Q_d = 0.05$. As depicted in Fig. 2, droplets are initially formed in a capillary tube (with a diameter, $D = 2.8$ mm) using a needle whose radius is and then polymerized in a narrower tube having a diameter, $d = 1.3$ mm.

volume and the diameter of the cylindrical tube. A simple way to perform this consists of connecting a tube having a diameter $d < 2r$ to the tube where droplets are generated (Fig. 1a) and exposing in this narrower tube the deformed droplets to UV radiation. As shown in Fig. 1a, because of the constriction the droplets adopt in the narrower tube a (sphero-cylinder) shape with a radius of the order of $d/2$ and a length L , which using the conservation of volume is roughly be given by $L = 4V/\pi d^2 + d/3$.

4. Conclusions

Our results clearly demonstrate that millifluidic-based synthesis is a very efficient strategy for the continuous production at extremely low cost of monodisperse polymer particles, in a size range from 100 to 2000 μm . The resulting particles feature extremely narrow size distribution (less than 2%) and a large versatility in dimensions, shapes and compositions. The size of the particles is controlled by varying the flow rates of the continuous and disperse phases, the design of the millifluidic reactor, namely the diameters of the central needle and that of the capillary tube. As for its microfluidic counterpart, the polymerization of polymer particles in millifluidic reactors presents two main features that distinguish it from other polymerization techniques such as batch polymerization or membrane emulsion. First, no stabilization against coalescence or Ostwald ripening of monomer droplets which are strong limiting factors for achieving a good monodispersity in size are required because their collisions in the millifluidic device are suppressed. Second, the shape morphology of polymer particles can be adjusted by tuning the constrained geometry of the millifluidic devices, leading to the production of rods, disks or more complicated shapes.

With no doubt, the millifluidic reactor, described herein, could also be used for the controlled synthesis of large inorganic or ceramic particles such as silica, titania or zirconia, the preparation of polymer large capsules or multiple emulsions. This will be the topic of a forthcoming paper by Tachibana et al. (in press). This method will also certainly find applications in cosmetology or food processing; two fields which often require the formulation of calibrated macroscopic disperse objects. However, the development of millifluidic-based synthesis of large objects will certainly require scaling up the particle production. This could easily be performed by associating several millifluidic reactors onto a single device. Considering that a single millifluidic reactor produces approximately 1 particles per seconds, a 50-reactors devices should produce up to 1.8×10^4 particles per hour.

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