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Polymerization-induced phase separation fabrication: A versatile microfluidic technique to prepare microfibers with various cross sectional shapes and structures

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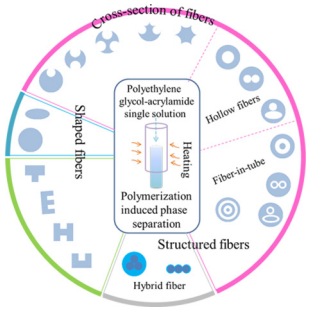
HIGHLIGHTS

- Polymerization-induced phase separation of AM/PEG solution occurs in microchannels.
- Shaped fibers are formed in microchannels with diverse cross-section shapes by PIPS.
- Single phase flow is used to fabricate various shaped PAM fibers.
- Fiber-in-tube fibers composed of different stimuli-responsive PAM are produced.
- Each fiber can be functionalized separately by adding different functional materials.

GRAPHICAL ABSTRACT



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ABSTRACT

Shaped microfibers have attracted great interests because of their broad applications. However, their preparation by microfluidic technique needs multi-phases by careful and accurate control of multi-flows. Here, we develop a simple polymerization-induced phase separation (PIPS) technique to fabricate microfibers with various cross-section shapes and structures. PIPS occurs when we transfer a single-phase flow of polyethylene glycol/acrylamide (PEG/AM) solution into a microchannel which is heated to initiate the polymerization of AM. This results in the formation of a polyacrylamide (PAM) core and a PEG solution layer between the microchannel wall and the core, thus facilitating the smooth spinning of the fibers and avoiding clogging of the microchannels. We designate microchannels with different shaped cross-sections to prepare PAM fibers which duplicate the shapes of the microchannels. In addition, we prepare fiber-in-tube fibers and biomimic fiber-in-matrice hybrid structures in the center of aligned capillaries. We use different acrylate monomers to prepare each fiber in the multiple-fibers, yielding fibers with stimulus responses. Further, each fiber can be functionalized by simple adding functional materials in the precursor solutions. This technique uses only a single phase solution and designated microchannels, providing a simple route to produce structured fibers with tailored shape and chemistry.

1. Introduction

Synthetic fibers are commonly produced with circular cross-sectional and homogenous structure. Recently we have witnessed an increasing demand on fibers with either non-circular

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cross-sections or heterogeneous structures or both. Such fibers exhibit exceptional properties which those circular-shaped or/and homogenous structure fibers cannot provide. Thus they can find broad application in areas like sound and heat insulating [1], sensors [2], separation [3] optical communications [4] biological [5,6] aspects, etc. On the other hand, many parts of the biological species are constructed by fibrous tissues with heterogeneous structures. The fibers composed of these tissues show abnormal cross-sectional shapes. And some of them are embedded in extracellular matrix, forming fibers-matrix hybrid structures, such as bundle of muscle fibers, collagenous fibers, and nerve fibers. Thus, synthesis of such biomimic hybrid structures needs techniques which can produce both various complex-shaped fibers and structures embedded with these fibers.

Several techniques have been developed to fabricate fibers with different morphologies, including standard spinning using spinnerets with shaped machined holes [7], electrospinning using a flow of polymer solution with a liquid-filled core [8,9], and microfluidic spinning [5,6,10–15]. Among them the first two techniques using generally single phase or simple two-phase solutions produce limited types of shaped fibers; while the microfluidic spinning technique exhibits versatility in the realization of a variety of complex cross-sectional shaped fibers, such as bamboo-like [10], spindle-knots [11], grooved flat [5], Janus [6,12] hollow [6,13] and multi-hollow [6,14] shape, thus attracting much attention.

Such realization is mainly accomplished by multiple, hydrodynamic focusing stream laminar multiphase microflow using channels with designed configurations or containing a sequence of pillars to sculpt the precursor solution into desired shapes [5,6,14]. The multiple stream laminar microflow can lead to the formation of simple hollow, semi-circular, spinner, ribbon-shaped fibers. The hydrodynamic focusing is able to fabricate more complex-shaped ones [16,17], including double anchor, diamond, triangle, U-shaped fibers. Nevertheless, multiple streams formed by using multiphase solutions have to be used in the microfluidic spinning technique. That is to say, the to-be-polymerized precursor-contained solution must be isolated so that it cannot contact the wall of the microchannel to avoid adhesion of the polymerized component to the wall, enabling smooth spinning. It is desirable to fabricate fibers with a wide range of cross-sectional shapes using a single phase solution by one type of the microfluidic spinning techniques. On the other hand, embedment of the shaped fibers in different materials, which mimics biological tissues, has not been produced in a one-step preparation procedure. Therefore, it is very interesting to develop such a procedure to realize these hybrid materials.

Recently, we discover that core/shell microdroplets can be easily formed from PEG/AM solution spherical microdroplets by PIPS, with PAM as the spherical core and PEG solution surrounding the core as the shell [18,19]. In this paper, we further find that polymerization of a flow of PEG/AM solution in a microchannel also results in phase separation of PAM form PEG, forming PAM fibers surrounded by PEG solution. And PIPS occurs in microchannels with any shaped cross-sections, resulting in PAM fibers with the cross-section shapes duplicated those of the microchannels. Such finding stimulates the idea of the fabrication of PAM fibers by microfluidic spinning technique using a single-phase precursor solution. Since the formed PAM fiber is surrounded by the PEG solution, it has no contact with the wall of the microchannel and can easily flow out of the microchannel, without worrying about clogging. The uses of the single-phase precursor solution provide many conveniences in operation over multiple phase microflows, thus enabling the fabrication of various-shaped and structured PAM fibers, hybrid fibers and embedment of the PAM fibers in other materials. We consequently designate microchannels by assembling simple plastic/glass capillaries with various diameters or carved channels on poly(methyl methacrylate) (PMMA) plates to form microchannels with various-shaped cross-sections. By introducing the PEG/AM solution in one or/and other capillaries, we can obtain PAM fibers with particular shaped cross-sections or structures. Furthermore, by introducing the PEG/AM solution in some capillaries and sodium alginate (AL) solution in other capillary, PAM-AL hybrid shaped fibers or AL ribbons with embedment of PAM fibers can be fabricated. Functionalization of the PAM fibers or each part of the hybrid materials is easily fulfilled in the fabrication of the fibers or materials. Such PIPS fabrication technique is versatile and is believed to enable the preparation of various kinds of microfibers with designed cross-section shapes using the system in which PIPS can occur in microchannels.

2. Experimental

2.1. Materials

AM, potassium persulfate (PPS), sodium alginate, isooctanol and acrylic acid (AA) were purchased from Sinopharm Chemical Reagent Corporation (Shanghai, China). PEG (M_w = 4000), n-hexane and liquid paraffin were obtained from Shanghai Lingfeng Chemical Reagent Corporation. N,N'-methylene bisacrylamide (MBAM) was purchased from Tianjin Chemical Reagent Research Institute. N-isopropylacrylamide (NIPAM), iron (II) chloride tetrahydrate, iron (III) chloride hexahydrate, sodium hydroxide and calcium chloride ($CaCl_2$) were obtained from Xiya Reagent Chemical Reagent Corporation. Potassium bromide (KBr), N-acetyl-L-cysteine, cadmium chloride, tellurium powder and Sodium borohydride were purchased from Aldrich. Polydimethylsiloxane (PDMS) was obtained from Dow Corning Corporation. The PTFE tubes and rods with different diameters were purchased from Chukoh Chemical Industries, Ltd. The glass capillary was obtained from West China University of Medical Sciences Instrument Industry. PMMA plate was purchased from Suzhou Yiguan plastic materials Industry. Syringe Pumps (LSP02-1B) used to introduce the solution into the microchannels were purchased from Baoding Longer Precision Pump Corporation. Magnetic Fe_3O_4 nanoparticles and $CdTe_{560}$ and $CdTe_{620}$ quantum dots were prepared as described in literature [20–22].

2.2. Experimental procedures

2.2.1. Preparation of solid fibers

Solid PAM fibers with conventional circular cross-section were prepared by pumping a PEG/AM aqueous solution into a commercial PTFE or glass capillary which was immersed in a 90 °C water or oil bath about 1–2 cm below the surface. The PEG/AM (or AA or NIPAM) aqueous solution was prepared by mixing 10 wt% of PEG-4000, 15 wt% of AM (or AA or NIPAM), 0.6 wt% of MBAM and 1.2 wt% of PPS in water. As the PTFE capillary is soft, we immobilized it by embedding it in a channel engraved on a PMMA plate, which was sealed with another PMMA plate by hot pressing. The suitable residence time for the polymerization was 25 s. When the PTFE capillary with 620 μm inner diameter (id) was used, the flow rate of the solution was 0.5 mL/h in water bath about 1.5 cm below the surface. After polymerization and phase separation, the aqueous phase was found to contain unconverted AM, PEG, and dissolved PAM [23,26]. To obtain the conversion of AM, we collected the fiber in a liquid paraffin bath in a fixed time, separated the aqueous phase from liquid paraffin, and measured the AM content in the collected aqueous phase by High Performance Liquid Chromatography. The result indicates that the AM content was 10.5 wt%. Thus the conversion of AM was 89.5 wt%.