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Ultralight, Soft Polymer Sponges by Self-Assembly of Short Electrospun Fibers in Colloidal Dispersions

*Gaigai Duan, Shaohua Jiang, Valérie Jérôme, Joachim H. Wendorff, Amir Fathi, Jaqueline Uhm, Volker Altstädt, Markus Herling, Josef Breu, Ruth Freitag, Seema Agarwal, and Andreas Greiner**

Ultralight polymer sponges are prepared by freeze-drying of dispersions of short electrospun fibers. In contrast to many other highly porous materials, these sponges show extremely low densities (<3 mg cm^{-3}) in combination with low specific surface areas. The resulting hierarchical pore structure of the sponges gives basis for soft and reversibly compressible materials and to hydrophobic behavior in combination with excellent uptake for hydrophobic liquids. Owing to their large porosity, cell culturing is successful after hydrophilic modification of the sponges.

1. Introduction

Natural sponges (*porifera*) are multicellular animals (*metazoa*) with large diversity and highly attractive properties not yet met by man-made substances.[1] For instances, natural sponges are lightweight materials with a density of 15 mg cm^{-3} (dried sponge) displaying excellent reversible compressibility. They can take-up large amounts of liquids and are excellent filters. Sponges with a volume of 1000 cm^3 can process up to 3000 L water h^{-1}. Furthermore, they can conduct light as discovered recently by Brümmer et al.[2] In addition, Natalio et al. reported on the formation of sponge skeletons shown to feature great bending strength and on the role of silicatein-α in the biomineralization of silicates in sponges, which accounts for the high reversible compressibility of sponges in spite of low densities.[3] Aizenberg et al. pointed out on the example of the so-called glass sponges (*Euplectella*) the important role of the hierarchical design from the nanometer to macroscopic length scale for structural materials.[4] The structural base of sponges are multiarmed spicules of silicate or calcium carbonate, which form highly porous structures of several hierarchical layers as shown in **Figure 1**A,B. This leads to highly porous ultralight 3D materials (ultralight is defined when the density of material is <10 mg cm^{-3}).[5] In recent literature, a variety of highly porous ultralight 3D materials were reported based on carbon, ceramics, and cellulose, which were characterized by porosities $>99\%$ and relatively high compressive strength.[6–10] Carbon and cellulose based sponges show ultralow densities and excellent mechanical properties but soft sponges with similar mechanical integrity are missing.

Since spicules of natural sponges conspicuously resemble polymer fibers, formation of such fibrous structures by electrospinning[11] could be a promising concept for the preparation of polymer-based biomimetic analogous of natural sponges and would open the huge potential of electrospun materials for 3D sponge-type structures. Indeed, 3D porous structures were prepared by electrospinning which was nicely summarized in comprehensive review in recent literature.[7] However, previous efforts of making 3D highly porous electrospun materials, for example, via ultrasonic treatment, resulted in higher densities and correspondingly lower porosities of $<99\%$,[12] as well as relatively poor mechanical performance. Remarkably, Eichhorn et al. claimed that theoretically ultrahigh porosities of electrospun nonwovens $>99\%$ could not be achieved.[13] In contrast to these reports, we present here the formation of ultralight weight highly porous 3D electrospun polymer fiber-based spongy structures with densities as low as 2.7 mg cm^{-3} corresponding to a porosity of 99.6%. They were prepared by electrospinning of a photo cross-linkable polymer followed by UV cross-linking, mechanical cutting, suspending cut fibers in liquid dispersion, and freeze-drying. These polymer sponges showed in analogy to natural

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G. Duan, Dr. S. Jiang, Prof. S. Agarwal,
Prof. A. Greiner
Macromolecular Chemistry II and Bayreuth
Center for Colloids and Interfaces
University of Bayreuth
Universitätsstrasse 30, 95440 Bayreuth, Germany
E-mail: greiner@uni-bayreuth.de

Dr. V. Jérôme, Prof. R. Freitag
Process Biotechnology
University of Bayreuth
Universitätsstrasse 30, 95440 Bayreuth, Germany

Prof. J. H. Wendorff
Department of Chemistry
Philipps-Universität Marburg Hans-Meerwein-Strasse
35032 Marburg, Germany

Dr. A. Fathi, J. Uhm, Prof. V. Altstädt
Polymer Engineering
University of Bayreuth
Universitätsstrasse 30, 95440 Bayreuth, Germany

M. Herling, Prof. J. Breu
Inorganic Chemistry
University of Bayreuth
Universitätsstrasse 30, 95440 Bayreuth, Germany

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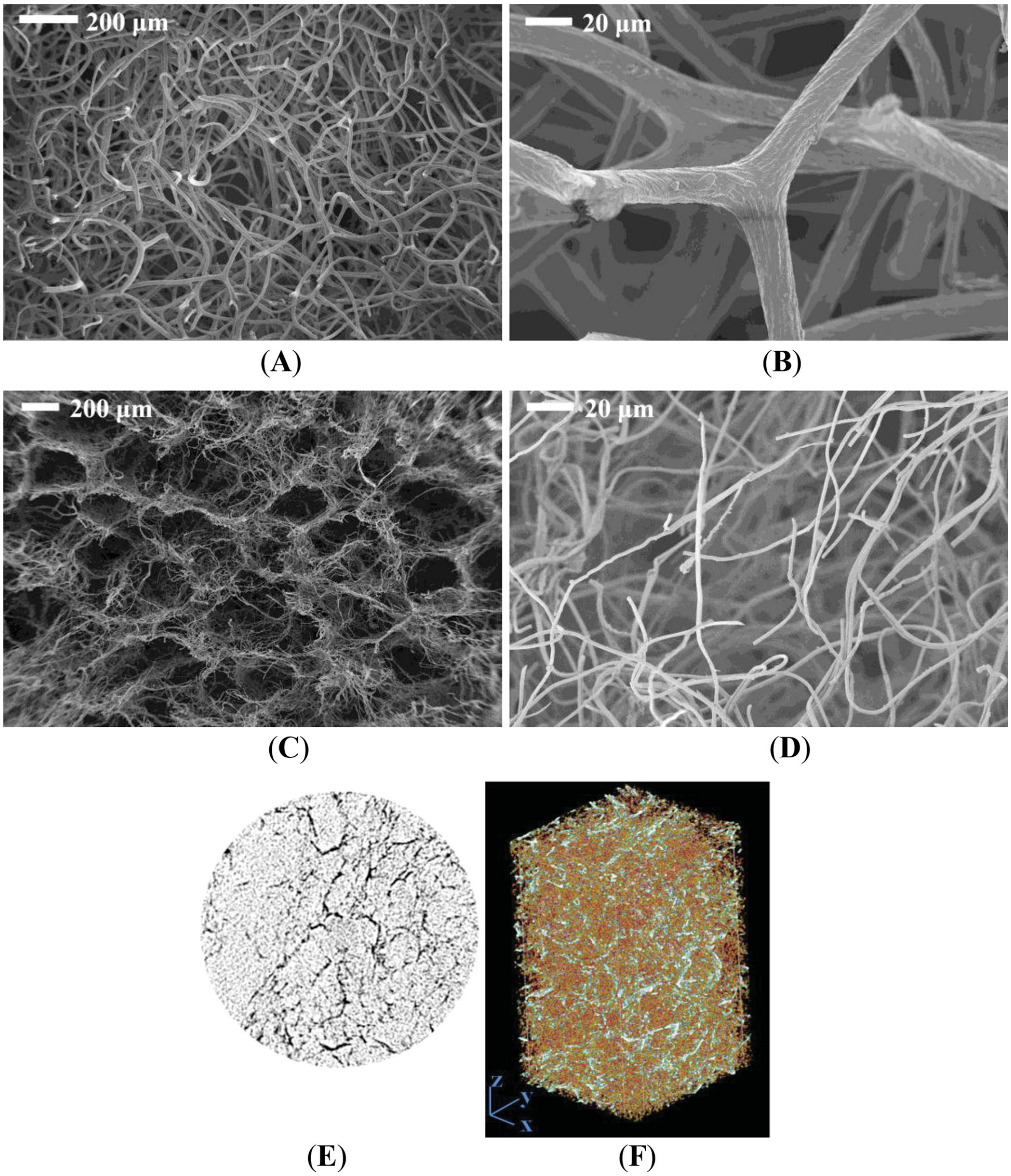


Figure 1. SEM images of A,B) a skeleton of a dried natural sponge (*spongia officinalis*) and of C,D) a polymer sponge prepared by freeze-drying of short electrospun fiber dispersion of cross-linked poly(MA-MMA-MABP). µ-CT analysis (sample no. 2) with top view, magnification: E) 60× and F) 3D side view, magnification: 90×.

sponges very good reversible soft compressibility and bendability without structural disintegration. Applications of these materials can be envisioned in a broad spectrum ranging from efficient filters and separation materials, functional construction materials (electrical, sound, or heat–cold insulation), scaffolds for tissue engineering, shape responsive materials, and confined catalysts.

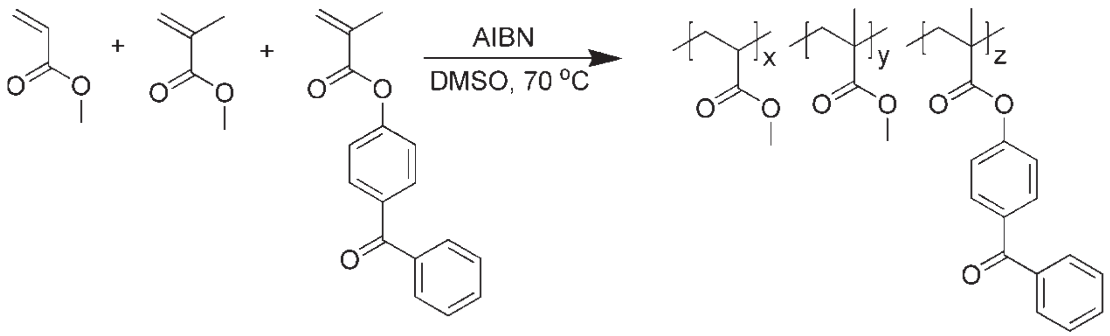
2. Results and Discussion

2.1. Preparation of Polymer Sponges

An acrylate copolymer with photo cross-linkable units (poly(methylacrylate(MA)-*co*-methyl methacrylate(MMA)-*co*-4-methacryloyloxybenzophenone(MABP) (poly(MA-*co*-MMA-*co*-MABP)), **Scheme 1**, details are given in Supporting Information) was synthesized and electrospun together with polyacrylonitrile (PAN) from pure DMF or a mixture of DMF, DMSO. As a result, fibers of different average diameters were obtained. Subsequently, dispersions of short electrospun fibers were prepared by cutting of the electrospun nonwovens of poly(MA-*co*-MMA-*co*-MABP) in dioxane in different concentrations. Sponges of different densities were prepared from these dispersions by freeze drying.

2.2. Structure and Mechanical Properties of Sponges

Based on the finding that dispersions of short electrospun fibers with high aspect ratio could form—under certain



Scheme 1. Preparation of poly(MA-MMA-MABP) from MA, MMA, and MABP by free radical copolymerization.

conditions—sponge-like structures combined with knowledge about the structure of natural sponges, we anticipate that percolation in combination with self-assembly played a significant role in the formation of man-made polymer sponge structure. Important for the formation of stable spongy structures after freeze drying was the use of short electrospun fibers with aspect ratio of 120–150 dispersed in dioxane. Obviously, porosity and density should correspond to the one defined by percolation threshold of fibers of a fibrillary structure with given length and radius. According to Berhan and Sastry,[14] the threshold can be represented for fibers with large aspect ratios by Equation (1)

$$\phi_c = \frac{V}{V_{ex}} \tag{1}$$

where ϕ_c is the volume fraction of the fibers. Here, the fibers are represented as capped cylinders. The volume V and excluded volume V_{ex} of such a fiber with length L and radius r is given by Equations (2) and (3)

$$V = \frac{4\pi r^3}{3} + r^2 \pi L \tag{2}$$

$$V_{ex} = \frac{32\pi r^3}{3} + 8\pi L r^2 + \pi L^2 r \tag{3}$$

For typical values of the system under consideration with L = 100 µm, r = 250 nm, we find ϕ_c = 0.00245 and a porosity $\varepsilon = (1 - \phi_c) = 0.9975$, which is close to the observed one of $\varepsilon = 0.9981$. In terms of predictions going from a radius of 250 nm to one of 25 nm, we estimate ϕ_c = 0.000249 and ε = 0.99975 ($\rho \approx$ 0.27 mg cm^{-3}) which are highly interesting values since these porosities and densities are close to the ones reported for record aerogels.[15] These calculations strongly support the experimental findings reported here for the sponge porosity. Analysis of the present polymer sponges by scanning electron microscopy (SEM) showed hierarchical order of the pores and interconnection of the fibers (fiber diameters in the range of 0.5–0.8 µm). Large pores of about 300–430 µm in diameter (Figure 1C) contained smaller pores of 10–30 µm (Figure 1D). The large pores could be attributed to the formation of crystals of frozen solvent formed in the freeze-drying process. The specific densities of the sponge were readily controlled by the concentration of the fibers in dispersion and by the average fiber diameter (Table S1, Supporting Information). The sponge density varied from 2.72 to 9.12 mg cm^{-3} on changing the short fiber dispersion concentration from 2.42 to 8.76 mg mL^{-1} for fibers with average diameter between 400 and 500 nm.

BET-surfaces of the present sponges generally were very low. For example, we measured a specific surface of 2.66 m^2 g^{-1} (determined with argon gas) for a sponge with a density of 3.75 mg cm^{-3}. According to micro-computer tomography (µ-CT), the fibers were homogenously distributed in the sponge (Figure 1E,F) which attributed to the integral stability of the sponge.

2.3. Properties of Sponges

Although the density of the sponge was extremely low, they could be handled manually without disintegration (**Figure 2**A–C). The compressive strength correlated with decreasing density of the sponge (Figure 2D). The Ashby plot of the compressive strength versus material density clearly revealed that electrospun polymer fiber sponges cover an important gap in this plot in comparison to other porous materials and are close to natural sponge (Figure 2E).

The high porosity of the sponge evidently has also significant effects on a variety of macroscopic properties. An illustrative example of macroscopic properties was the uptake of mineral oil from water. In these experiments, we found that the oil was taken up selectively from water in less than a minute as soon as the present sponge came in contact with the liquid phase (**Figure 3**A). After complete uptake of oil it was still shape persistent (inset in Figure 3B). Interestingly, with sponge sample no. 1 of lowest density (2.72 mg cm^{-3}, Table S1, Supporting Information), the weight of mineral oil in the sponge closely corresponded to the density of the mineral oil itself and, thereby, close to 30 000% of the weight of the pure sponge. This indicates the role of a fiber network in the sponge-like material for the stabilization of the liquids which compares to the role of collagen nanofiber networks in natural tissues. Interestingly, the as prepared sponges were hydrophobic (Figure 3B), which makes them of interest for membrane applications.

The liquid absorption capacity of the electrospun freeze dried sponges was inversely proportional to their densities (Figure 3C), which indicates pore filling as mechanism for oil uptake rather than surface wetting. Similar behaviour for selective uptake of other hydrophobic organic liquids from water was observed (Figure 3C). For instances, reversible sorption and desorption of cyclohexane was found (Figure 3D). Importantly,

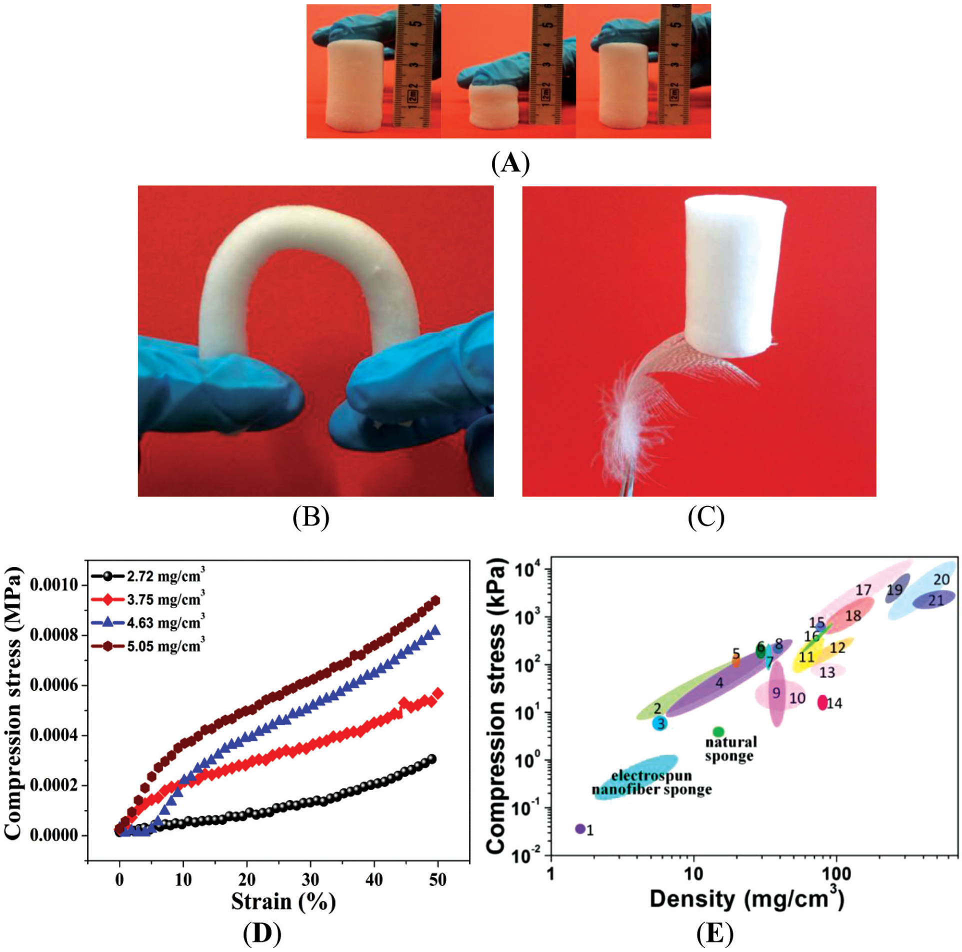


Figure 2. A) Reversible manual compression, B) bending test, C) demonstration of ultralight weight of a present electrospun/freeze dried sponge (sample no. 3), D) compression test of sponges of different densities, and E) Ashby plot of sponge compressive strength versus density for different materials. 1) Boron nitride,[9] 2) carbon nanotube,[6] 3) carbon aerogel,[15] 4) cellulose fiber,[16] 5) cross-linked polystyrene,[17] 6) polyolefin (closed cell),[18] 7) polyethylene (closed cell),[19] 8) polyimide,[20] 9) polyethylene (50% strain),[19] 10) silk fibroin,[21] 11) melamine-formaldehyde (rigid),[22] 12) tannin-based (rigid),[23] 13) PDLLA/Bioglass composite,[24] 14) latex rubber,[19] 15) PAN-microspheres and fibers,[25] 16) rigid polyurethane,[26] 17) PVC (cross-linked),[27] 18) epoxy-boroxine,[28] 19) bio-based macroporous polymers,[29] 20) silicon oxycarbide ceramic,[30] and[21]) aluminum foams.[31]

when the procedure was repeated several times, no loss in efficiency was observed. It should not remain unmentioned here that similar liquid uptakes were reported for other ultralight 3D structures,[6,10] however observed with other materials than man-made polymers.

2.4. Application of Electrospun Sponges

3D nanostructured materials are also of interest for other applications such as for filtration, mechanical damping, catalysis, and cell–material biointerface design.[32] High porosities are required for the successful growth of cells in materials. In contrast to known ultralight high porosity materials, the mechanical softness of the present polymer sponges and its potential for chemical and biological functionalization is of major interest for cell tissue formation. In order to explore whether cells could grow in the present polymer sponges, Jurkat cells, which were used previously in cell electrospinning, were brought into contact with the sponge. Before contact the sponges were coated with poly(vinyl alcohol) in order to provide sufficient hydrophilicity for contact with cell culture media. After 2 d of incubation, the cells have formed cell clusters with the sponge (**Figure** 4A). SEM revealed that clusters of cells grew on to the fibers of the sponge and cells adhered to the fibers (Figure 4B). Viable cells were found inside the sponge by confocal microscopy after 13, 20, and 30 d of culture, indicating significant cell growth (Figure 4C–E). L929 cells gave similar results but are not reported here in detail.

3. Conclusion

In conclusion, ultralight highly porous 3D polymer sponges of extremely low density and low specific surface area were obtained from dispersions of short electrospun fibers in an attempt to mimic the design principle of natural sponges.

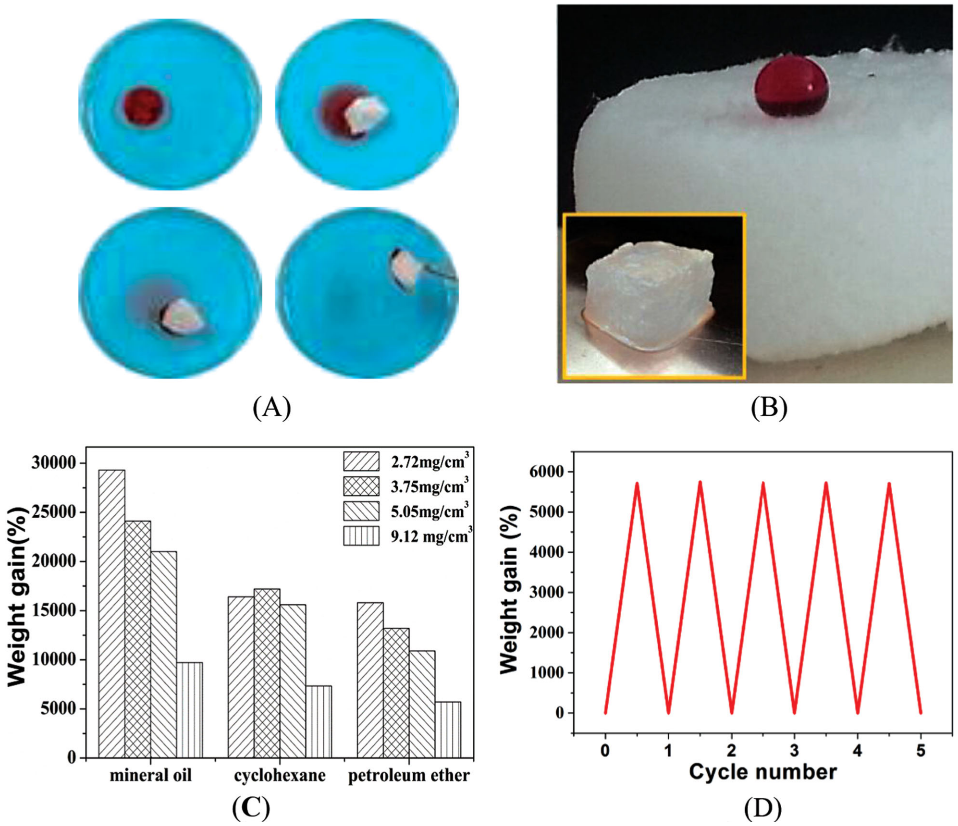


Figure 3. Liquid uptake by polymer fiber sponges. Photographs of A) mineral oil (dyed by Sudan red) uptake from water, B) one drop of rhodamine B dyed water on the top of sponge sample 7 (inset shows shape persistent sponge completely soaked with mineral oil (1.2 cm × 0.9 cm × 0.85 cm)). C) Uptake of hydrophobic liquids from water in wt% as a function of sponge density. D) Reversibility of cyclohexane uptake (sample 4, $\rho = 9.12$ mg cm^{-3}), after uptake cyclohexane was evaporated for deloading the sponge.

The porosity of the polymer sponges obtained from the dispersions of short electrospun fibers produced by subsequent freeze drying could be understood by the classical percolation theory. Remarkably, the pore morphologies of the sponge featured hierarchical order for reasons currently not yet understood, but which could account to the surprisingly good reversible compressibility and bendability, given their low densities, which was also confirmed by the recent contribution of Ding et al.[33] The mechanical properties of the novel polymer sponges close an important gap in an Ashby plot of compressibility versus density. It should not remain unmentioned that the compressive strength of the sponge could be tailored with negligible loss in porosity by several coating techniques which are presently under investigation in our lab. In contrast to many other highly porous materials, the present sponges prepared by electrospinning/freeze-drying gain functionality pore filling rather than surface wetting, which opens completely new perspectives for functional materials. Given the wide variety of polymers that can and have been electrospun into filaments combined with the formation process presented here, such sponge materials will enable the design of many new functional materials ranging from ultralight materials to membranes, filters, insulators, electrodes, and scaffolds for biomedical applications.

4. Experimental Section

All experimental details regarding polymer synthesis, characterization, UV cross-linking, sponge densities, cell studies are provided in Supporting Information.

Electrospinning of Fibers: Solutions for electrospinning were prepared by dissolving 8.0 g of poly(MA-*co*-MMA-*co*-MABP) and 1.0 g of PAN in a mixture of solvents (31.0 g of DMSO, 6.5 g of DMF and 1.8 g of acetone; total polymer concentration = 18.6 wt%). Another solution for electrospinning with polymer concentration of 20 wt% was prepared by dissolving poly(MA-*co*-MMA-*co*-MABP) (8 g) and PAN (1 g) in pure DMF (36 g). The conditions used for electrospinning were: electric potential 12 kV, flow rate 1.8 mL h^{-1}, and a distance between the electrodes of 13.0 cm. The electrospun fibers were collected in the form of a nonwoven on a grounded rotating drum (diameter 20 cm) with a rotating speed of 20 rotations per minute.

Preparation of Electrospun Fiber Dispersion: The electrospun fiber nonwoven was first dried in vacuum oven at room temperature for 3 d and then irradiated under UV light (UV lamp 250 GS) with a distance of 15 cm for 5 h. Afterward the cross-linked nonwoven was cut into short fibers in dioxane with a mixer at a rotation speed of about 5000 rpm for 45 s. Short fiber dispersions with different concentrations (Table S1, Supporting Information) were prepared by controlling the weight ratio of fiber nonwoven in the dispersion and the volume of the dispersion solvent, here dioxane.

Preparation of Polymer Sponges: The above short fiber dispersions were freeze-dried in cylindrical glass vials for 48 h to yield sponges with different densities (Table S1, Supporting Information).

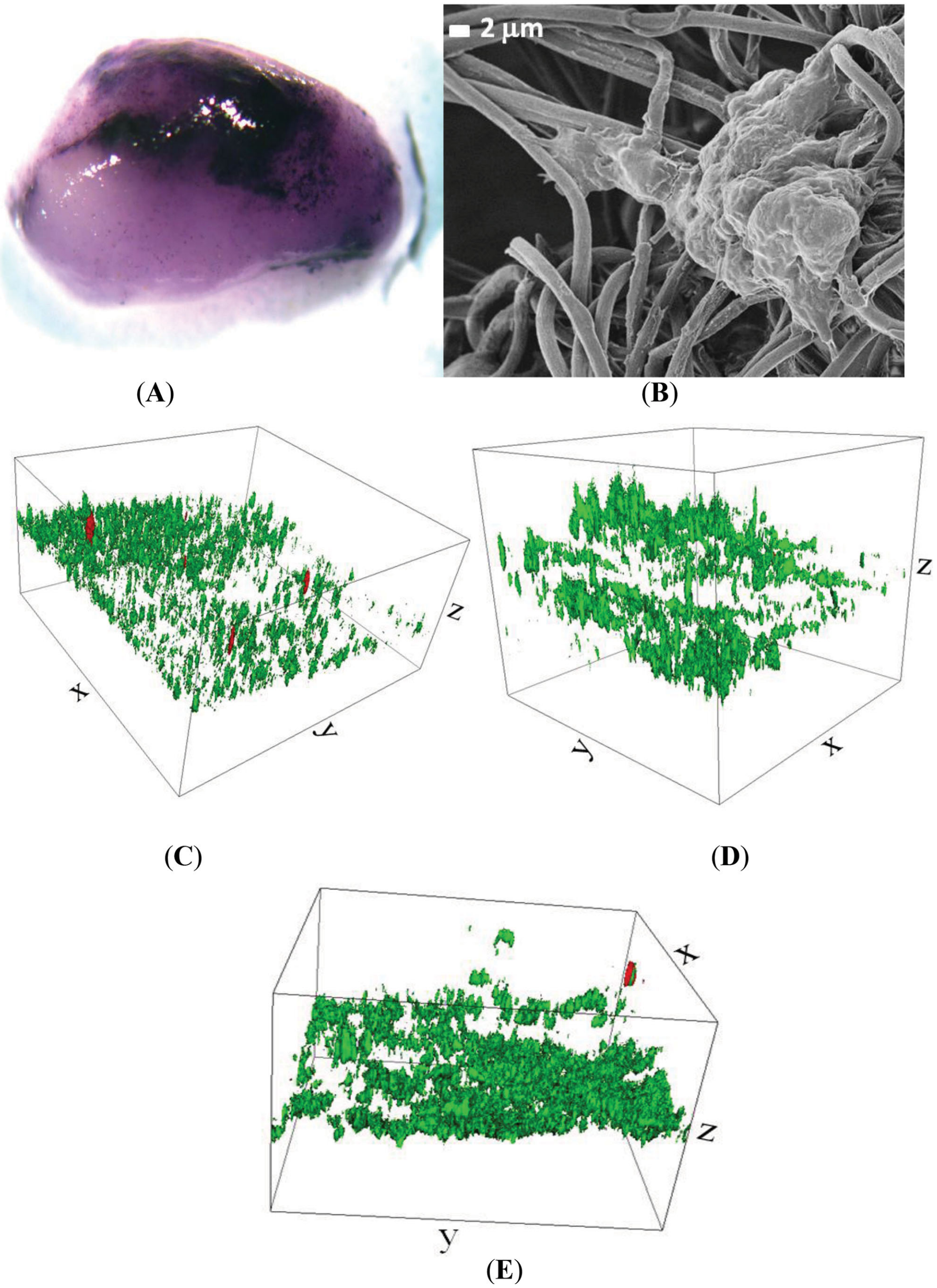


Figure 4. Cell growth in electrospun/freeze dried polymer fiber sponges. A) Image (MTT staining, long axis of the sponge is about 5 mm) and B) SEM photo of Jurkat cells colonized on a sponge (sample no. 2) after 2 d of colonization. 3D confocal microscopy of live (green) and dead (red) Jurkat cells in sponge (sample no. 2 after 13 d (C) ($x \times y \times z = 450 \times 450 \times 250$ µm), 20 d (D) ($x \times y \times z = 450 \times 450 \times 400$ µm), and 30 d (E) ($x \times y \times z = 450 \times 450 \times 300$ µm) of cells incubation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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