Electrospinning of Highly Aligned and Covalently Cross-Linked Hydrogel Microfibers

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ABSTRACT: Smart polyelectrolyte hydrogels are increasingly studied toward the realization of soft microactuators. This study focuses on the fabrication of highly aligned and covalently cross-linked polyacrylamide hydrogel microfibers by electrospinning technique following two-stage polymerization. The engineering of the reaction timescale of the precursor, such that the material gels shortly after spinning, is described and the design of the electrospinning setup, to generate highly aligned fibers, is presented. In addition the effect of the operating parameters on the fibers average diameter is investigated. The generated fibers are 15 cm long with average diameter ranging between 100 nm and 1.10 μm. The fibers diameter is controlled by adjusting the thickener type and concentration in the precursor and the electrospinning processing parameters. Thinner fibers are generated at lower thickener molecular weights and concentrations as well at lower flow rate and higher voltage. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41092.

INTRODUCTION

Electrospinning provides a user-friendly approach to fabricate nanoscaled to microscaled fibers. The conventional setups generate randomly oriented fibers in the form of nonwoven mats.[1–4] But it is desirable to generate ordered structures to broaden the applications of the fibers. There have been a few approaches to improve the orderliness of electrospun fibers.[5–8] Yet there is no previous study reporting the production of well-aligned and covalently cross-linked hydrogel microfibers.

Open literature shows that more than 200 different polymers have been successfully electrospun into ultrafine fibers for various applications and the number is still increasing gradually. Most of the polymers were dissolved in some solvents before electrospinning but they do not derivate from a monomers pre-gel solution.[9]

Cross-linked polyacrylamide (PAAM) hydrogel is a biocompatible[10,11] actuating and sensing polyelectrolyte that adapt and respond to physicochemical, electrical, and biochemical stimulations.[12–16] It is the most suitable material to be used in mimicking the biological muscle.

The main problem of PAAM actuators is their prohibitively slow actuation rate since the diffusion time in Bulk hydrogels is inversely proportional to the square of the diffusion distance.[17] Thus, a successful muscle-like actuator will need to replicate the small scales of the muscle fibers that achieve fast response.

Therefore, the fabrication of well-aligned and highly ordered hydrogel microfibers is strongly needed to use them into a complex muscle architecture.[16,18] The fibers micrometer scale improves mechanical properties[19] and the time of response of the device.[15,18,20] If these conditions are met, the fabrication of an artificial muscle with strength and speed matching and even greater than that of a human muscle may be possible by assembling a large number of small elements acting in parallel.[16]

In a previous study, we reported the electroactivity of PAAM hydrogel muscle-like actuators that mimic the natural muscle in form and motion. The fibers micrometer size enables them to exhibit instantaneous response and a tunable electroactivity with a 2D control of position at low driving voltage. For the first time in the field of smart hydrogel, the electroactive hydrogel microactuators are driven by electrostatic forces instead of pH variation. These outstanding properties make them optimal candidates for many important applications in particular as functional units for the development of synthetic replacements for active biological tissues[21] (see videos in supporting

Table I. Composition of Different Thickeners

Thickener	Composition			Molecular weight (g/mol)
	AAM	APS (μL)	TEMED (μL)	
LT30	1 mL AAM (30 wt %)	5	1	7.8×10^6
LT15	1 mL AAM (15 wt %)	5	1	8×10^5
LT7.5	1 mL AAM (7.5 wt %)	5	1	3.2×10^5

Information). It also opened a new door to new applications such as gel-based soft machines, biosensors, materials for microfluidic devices, scaffolds for tissue engineering and wound dressing applications.[22,23]

In this article, we focus on the research effort used in the improvement of the electrospinning process that is based on the classical techniques but with some modifications. In fabricating our one-dimensional polyelectrolyte fibrous structures, we faced two main challenges: The first challenge was the generation of long and linearly arranged microfibers that are ready to be used directly in future complex structures, and the second challenge was the spinning of chemical gels before the gelation reaction could form covalently cross-linked fibers.

We have overcome these challenges following two-stage polymerization by adapting the chemical composition of the electrospinning precursor solution to permit its spinnability, as a first stage. The precursor solution consists of a pre-gel solution to which we added linear PAAM gel of different molecular weight as thickener. The reaction time of the pre-gel solution was controlled by slowing down the rate of its polymerization reaction. The second stage consists of annealing the obtained fibers for full polymerization.

In addition, we designed a new electrospinning apparatus that generates highly aligned ultrafine fibers spread over large areas making it possible to efficiently and economically produce fiber-based devices. Several parameters of the electrospinning process are varied and the correlation between the setup parameters and the resulting microfibers diameter is investigated.

This comprehensive study reports in detail the steps followed in engineering the reaction time scale of the precursor such that the material transforms into a gel shortly after spinning, and modifying the electrospinning setup such that long and highly aligned fibers are obtained. Through this approach, this article can contribute to increased control of the electrospinning process and, thus, enhanced applicability.

EXPERIMENTAL

Acrylamide 99% (AAM), TEMED N,N'-tetramethylenediamine (99%), bisacrylamide (BIS) N,N'-methylenebisacrylamide (98%), and ammonium persulfate (APS; 98%) are used. All chemicals were purchased from Aldrich and used as received without any further purification. Deionized water was used for all the dilutions, polymerization reactions, and swelling. Aqueous solutions of the monomer AAM (30, 15, and 7.5 wt %), the cross-linker BIS (2 wt %), and the initiator APS (25 wt %) were prepared.

The electrospinning precursor consists of a pre-gel solution prepared by mixing (AAM, BIS, APS, TEMED) to which we added linear PAAM gel (LPAAM) as a thickener.

Three thickeners of different molecular weights are prepared. Their composition and molecular weight are shown in Table I. The preparation of different precursors is discussed in details in the following section.

The molecular weight is measured by chromatography using "Waters 510" pump, a refractometric detector "Gilson 132," and a light scattering apparatus Dawn DSP "Wayatt Technology." The chromatographic column is filled with "PL Aquagel OH-mixed," the buffer used is sodium phosphate 0.01 M, NaCl 0.15 M, pH = 7. The temperature of the pre-gel mixture is measured using a digital thermometer (Lutron TM-917) attached to a thermocouple Pt100 and connected to the computer with a RS232 cable using the software Lutron 801 (Version 080117). The temperature profiles are registered at a rate of 1 point each 5 s with a precision of 0.1°C. The viscosity is measured using AR-G2 rheometer (TA Instruments). The fibers diameters are measured using scanning electron microscope (Seron Technology AIS2100). Each data point corresponds to the average diameter value calculated for 40 fibers measured for each experimental condition. The diameter distribution is among the 10% of the average value.

RESULTS AND DISCUSSION

Precursor Preparation
The first challenge faced was the preparation of the electrospinning's precursor that can be spun into fiber and then polymerized to form covalently cross-linked gel.

It was essential to undergo a rheological characterization prior to processing the pre-gel solution with electrospinning to
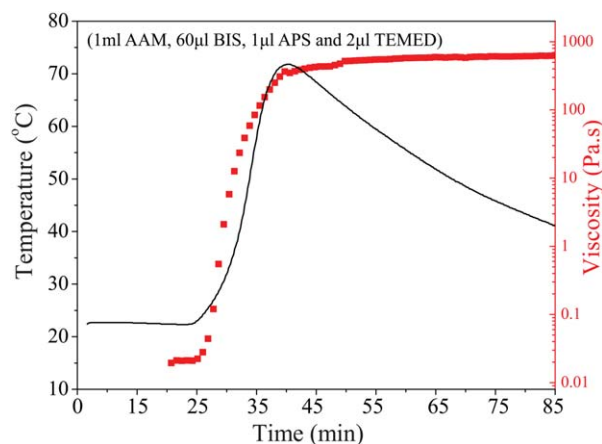

Figure 1. Reaction kinetics: Variation of the temperature (solid line) and viscosity (square) of the pre-gel solution registered as function of time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
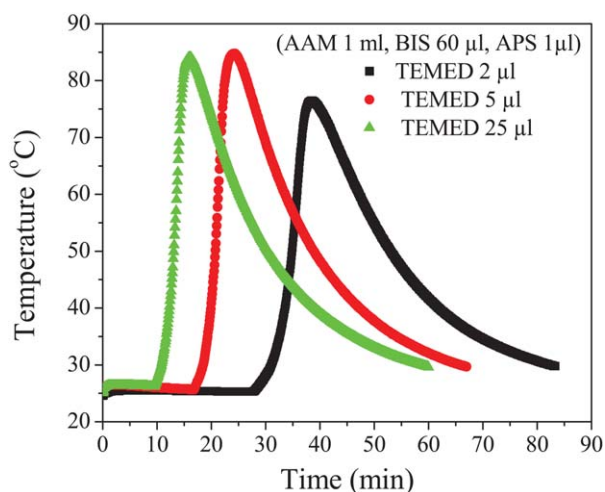
Figure 2. Graph showing the variation of the temperature versus time of different pre-gel solutions containing different amount of TEMED. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

correlate spinnability with the material's rheological properties as it transform from a sol to a gel.

Figure 1 shows the reaction kinetics in terms of temperature and viscosity. It is clear that before the starting of the polymerization reaction the pre-gel cannot be spun due to its low viscosity. Then, when the polymerization starts, its viscosity increases rapidly to reach the maximum or the "gel point" where the macrogelification occurs. Which will leads to the obstruction of the spinneret during the electrospinning.[24–26] Strategically, delaying the polymerization of the pre-gel solution by using low concentration of the initiator APS and the accelerator TEMED, and adding the thickener (linear PAAM gel) to increase its viscosity, allows the spinning of the pre-gel into fibers before the gelation.

The temperature profiles of pre-gel solutions having the same amounts of AAM 30 wt % (1 mL), BIS 2 wt % (60 μL), and

APS 25 wt % (1 μL) but different amounts of the accelerator TEMED (0.2, 0.5, and 2.5 μL TEMED) are registered. Figure 2 shows that when the concentration of TEMED increase the polymerization begins earlier and gel point is achieved faster. The concentration of 0.5 μL of TEMED for each 1 mL of AAM was selected, since the polymerization started after 23 min which gives a large timeframe to spin the solution before the starting point of the polymerization. For lower concentration of TEMED, the obtained fibers were difficult to polymerize.

Thus, the precursor solution consists of a pre-gel solution to which we add one of the three thickeners. Nine different precursors were selected; their composition is presented in Table II. Figure 3 shows a schematic representation of different precursors.

Electrospinning Apparatus

The second challenge faced was the generation of highly aligned fibers. Thus, a new electrospinning setup was implemented to obtain well oriented fibers that are ready to be used in complex devices.[16,21]

The electrospinning setup [Figure 4(a)] consists of a 100 × 60 × 60 cm³ Plexiglas box that contains a spinneret, a collector, and an air gun. The electric field is controlled by a high voltage power supply (Leybold 521721). The flow rate of the precursor solution is controlled by a syringe pump (B. Braun Perfusor compact, Syringe driver) connected by a silicone tube to a non-oxidizable steel spinneret (I&J Fisnar, Stainless Steel Dispensing Tip, gauge 20). The spinneret is fixed on the upper side of the Plexiglas box. The collector is formed by two square frames of aluminum of 30 cm sides placed horizontally, separated by a gap of 15 cm, which could be adjusted to control the fiber length. A copper wire connects the two frames, thus, maintaining them at the same electric potential. Plastic rods fix the distance between the two frames and hold the collector. The temperature inside the box is controlled by a hot air gun (Black and Decker type 3) connected to a digital temperature controller (Electrothermal MC 810). The air gun is introduced at the bottom of the box at 60 cm from the spinneret.

Table II. Composition of the Different Precursors

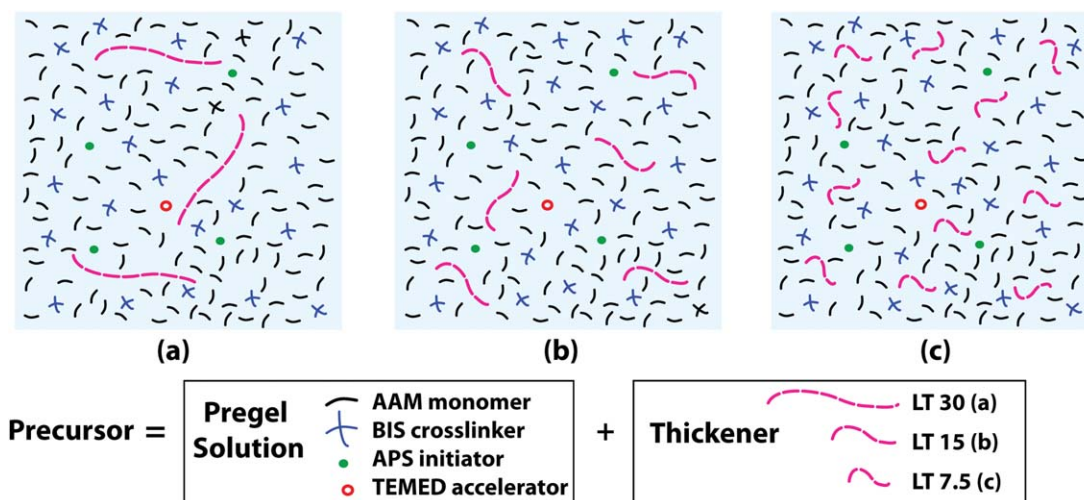| Precursor	Thickener (g)	Pre-gel solution				
		Water (g)	AAM (g)	BIS (mg)	APS (mg)	TEMED (μL)
	LT30					
A1	13	87	30	120	25	50
A2	8	92	30	120	25	50
A3	5	95	30	120	25	50
	LT15					
B1	50	50	30	120	25	50
B2	30	70	30	120	25	50
B3	26	74	30	120	25	50
	LT7.5					
C1	100	0	30	120	25	50
C2	62.5	37.5	30	120	25	50
C3	55	45	30	120	25	50

Figure 3. Schematic representation of three precursors having the same AAM content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The new setup originality lies in the combination between the shape of the collector, its position relative to the polymer jet and the use of air flow. The collector conducting frames placed in parallel and electrically connected together stretch the polymer by splitting the main jet into several sub-jets of thinner diameters. The control of the temperature inside the box allows
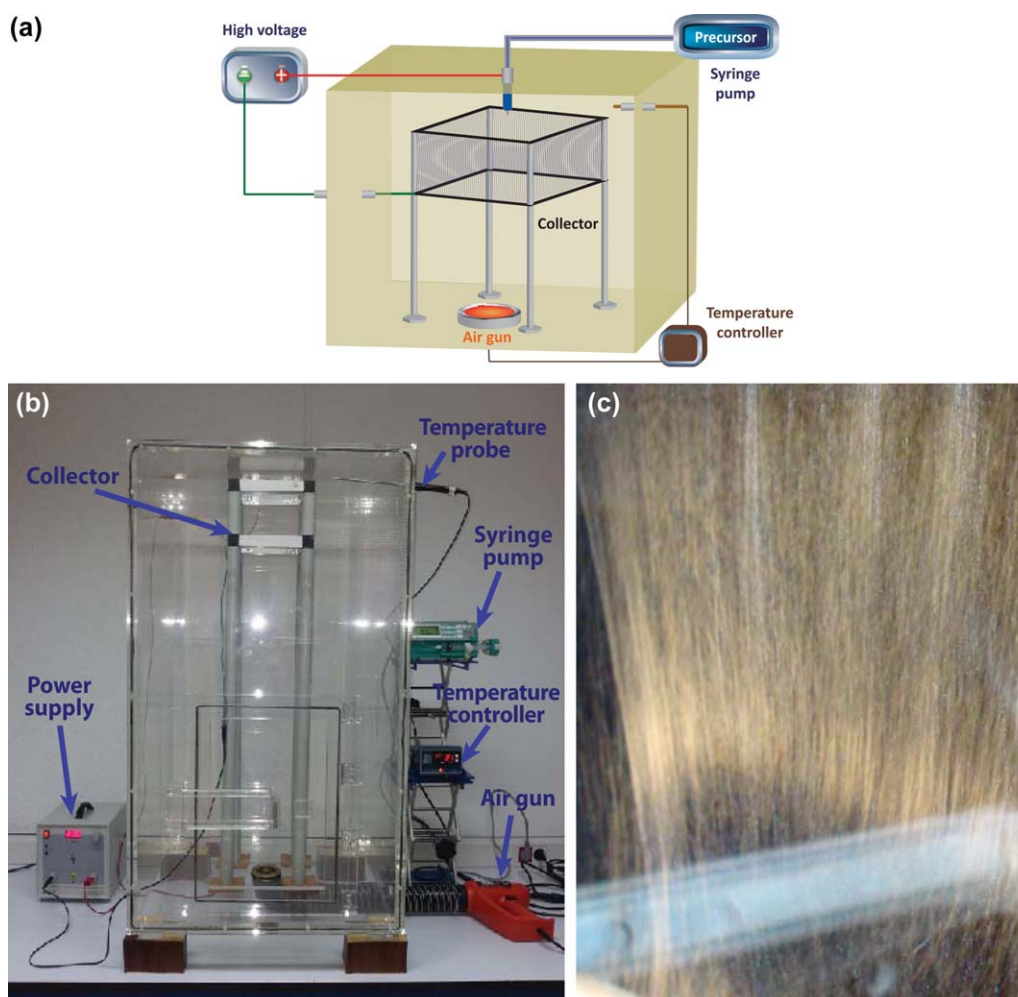
Figure 4. (a) Schematic representation of the electrospinning setup, (b) Picture of the electrospinning setup, and (c) Picture of the resulting fibers highly aligned between the two collector's frames. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
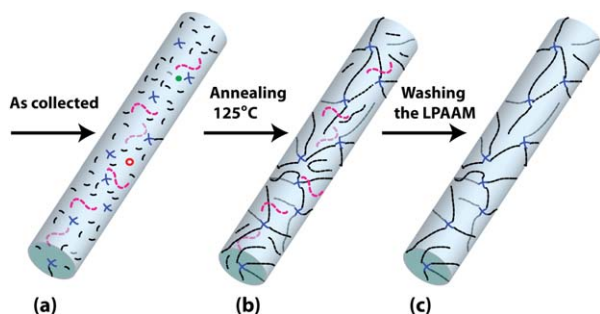
Figure 5. Schematic representation of a microfiber (a) as collected (b) after annealing (c) after washing and the remove of the uncross-linked segments and the thickener. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

controlling the solvent evaporation rate. In the absence of the air gun, the fibers will remain wet due to the short distance between the jet and the collector, and therefore, stick to the frame. Thus, the airflow adjusts the distribution of the fibers and evaporates the solvent, which is an important factor in keeping the potential at the collector constant and avoiding short circuits between the spinneret and the frames.

Once the electric field is applied, the polymer jet is stretched and refined into fine fibers. The fibers align to minimize the net torque of electrostatic forces and the self-assembled fibers dried instantaneously and grow vertically in parallel between the two collector's frames [Figure 4(c)].

Fibers Activation
Afterward, the highly aligned fibers are collected and annealed for 4 h at 125°C to assure full polymerization into a three-dimensional network. The microfibers are then washed with distilled water to allow the linear PAAM embedded within their structure and the uncross-linked polymeric chains to diffuse outside the fibers. Then, the microfibers are hydrolyzed in 1 M NaOH solution and washed with distilled water until they reach the full swelling (Figures 5 and 6).

The fibers are electroactive,[21] porous, and have a well-defined microstructure. They do not dissolve in water which confirms the covalent nature of the network.

Effect of the Operating Parameters
The effect of flow rate, applied voltage, type, and concentration of the thickener in the precursor is studied under constant temperature of 60°C being the optimal temperature for the evaporation of the solvent.

The precursor viscosity is an important parameter that influences its spinnability. Thus, the thickener's molecular weight and concentration in the precursor determines its limiting boundaries or the threshold of being electrically spun. Using the thickener LT30 precursors having a 2% to 13% content of thickener can be electrospun. Precursors having 26% to 50% content of thickener LT15 can be electrospun. Precursors having 55% to 100% content of thickener LT7.5 can be electrospun.

The boundary conditions for different type of thickeners show that precursors containing thickeners of different molecular weight have different spinnable concentration ranges. In addi-

tion, the usage of a high molecular weight thickener is not essential for fibers generation if sufficient intermolecular interactions can provide a substitute for the interchain connectivity obtained through chain entanglements.

Lower thickeners' concentration solutions form droplets that cannot be stretched into fibers, due to the capillary breakup of the spinning jet by surface tension. While higher thickeners' concentrations prohibit fiber formation due to higher values of viscosity. As it was reported in other studies,[27] pumping the solution through the syringe pump becomes very difficult, and the solution dry at the tip of the spinneret.

The effect of LT30 thickener concentration on the fibers average diameter and the precursor viscosity are shown in Figure 7 formed under a voltage of 15 kV and a flow rate of 10 mL h^{-1}. It is clear that the fibers average diameter increases linearly as the thickener concentration increase. We should note that bead-on-fiber morphology was obtained for the thickener concentration of 2%. This is attributed to the poor chain entanglement density in the solution and insufficient resistance to the electrostatic field. When the concentration becomes higher than 3% smooth fibers were generated.
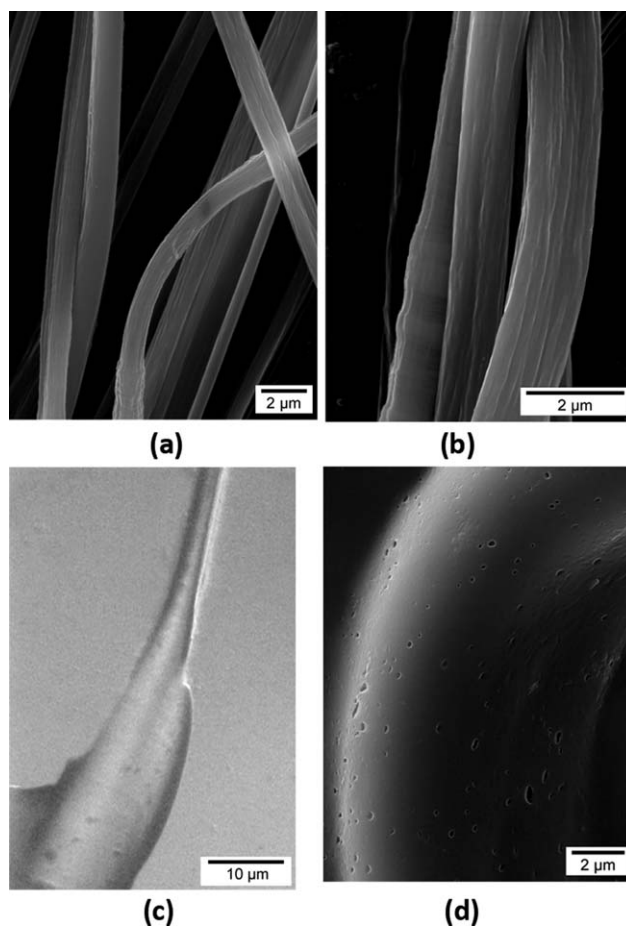

Figure 6. SEM images of the resulting microfibers (a) and (b) as collected, (c) during the swelling, and (d) after swelling and the removal of the thickener. Fibers derived from precursor "A1" spun under a voltage of 15 kV and flow rate of 25 mL h^{-1}.
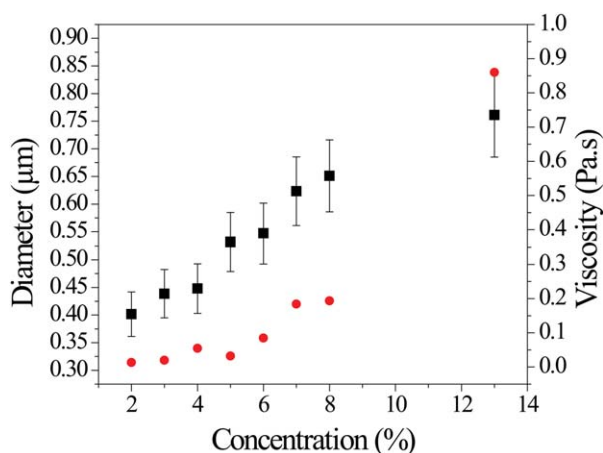
Figure 7. Effect of the thickener LT30 concentration on the average diameter of electrospun fibers at a potential difference of 15 kV and flow rate of 10mL h^{-1}; the red dots show the viscosity for different concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The flow rate of the precursor is an important process parameter in determining the fibers average diameter. This correlation is evaluated under 15 kV for the nine different precursors. The results presented in Figure 8 show that by varying the flow rate from 5 to 25 mL h^{-1}, fibers with diameters ranging from 400 nm to 1.1 μm are obtained using the thickener LT30, while fibers with diameters ranging from 220 nm to 0.84 μm are obtained using the thickener LT15 and fibers with diameters ranging from 190 nm to 0.41 μm are obtained using the thickener LT7.5.

The fibers average diameter increases linearly with the flow rate regardless of the precursor type as it influences the jet velocity and, therefore, the amount of solution available for electrospinning. This behavior is similar to others studies found in literature.[28,29]

The variation of fibers diameter under different applied voltages is evaluated at a flow rate of 10 mL h^{-1} and for the nine different precursors. It is shown (Figure 9) that an increase of the applied voltage leads to a decrease in the diameter of the electrospun microfibers regardless of the precursor type. By varying the applied voltage from 10 to 25 kV, fibers with diameters ranging from 0.85 μm to 320 nm are obtained using the thickener LT30, while fibers with diameters ranging from 0.61 μm to 280 nm are obtained using the thickener LT15 and fibers with diameters ranging from 0.41 μm to100 nm are obtained using the thickener LT7.5.
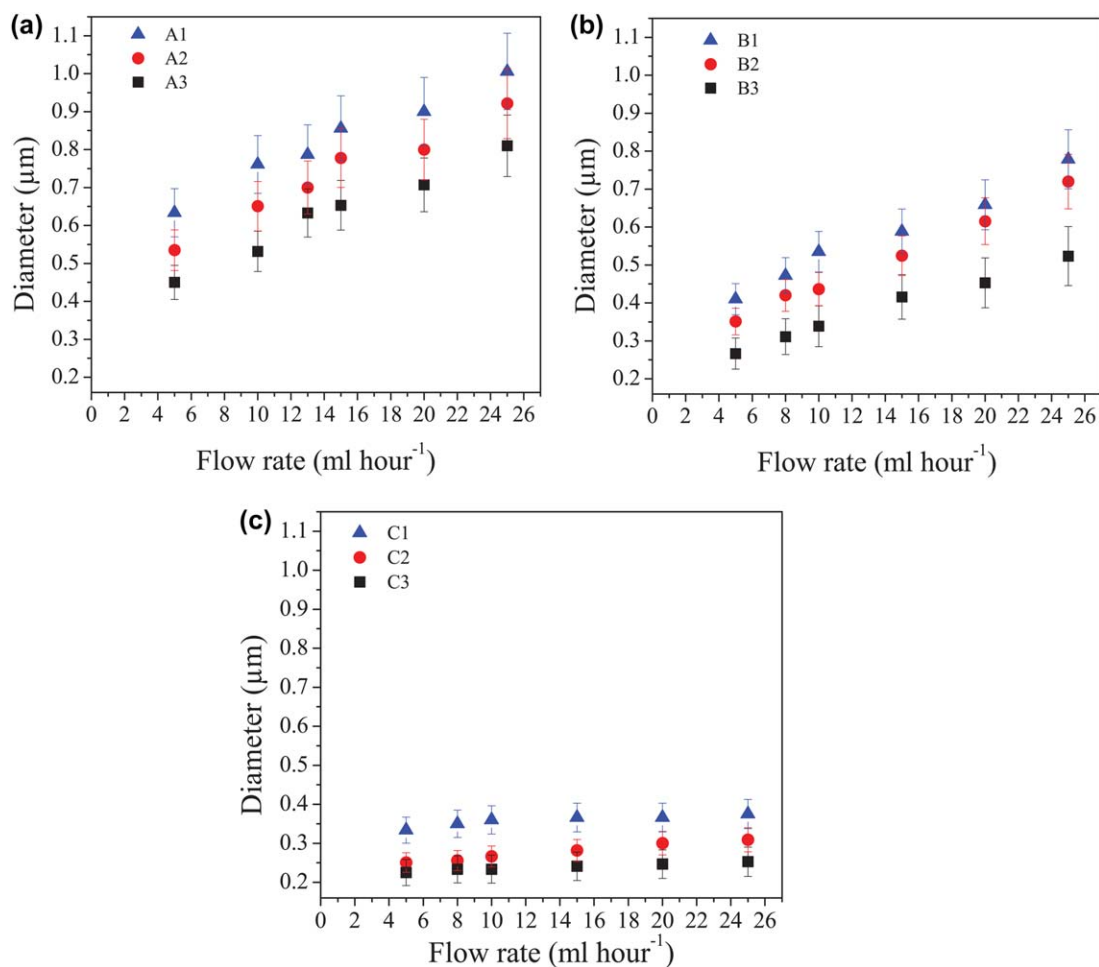

Figure 8. Effect of the flow rate on the average diameter of electrospun fibers at a voltage of 15 kV for different precursors. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
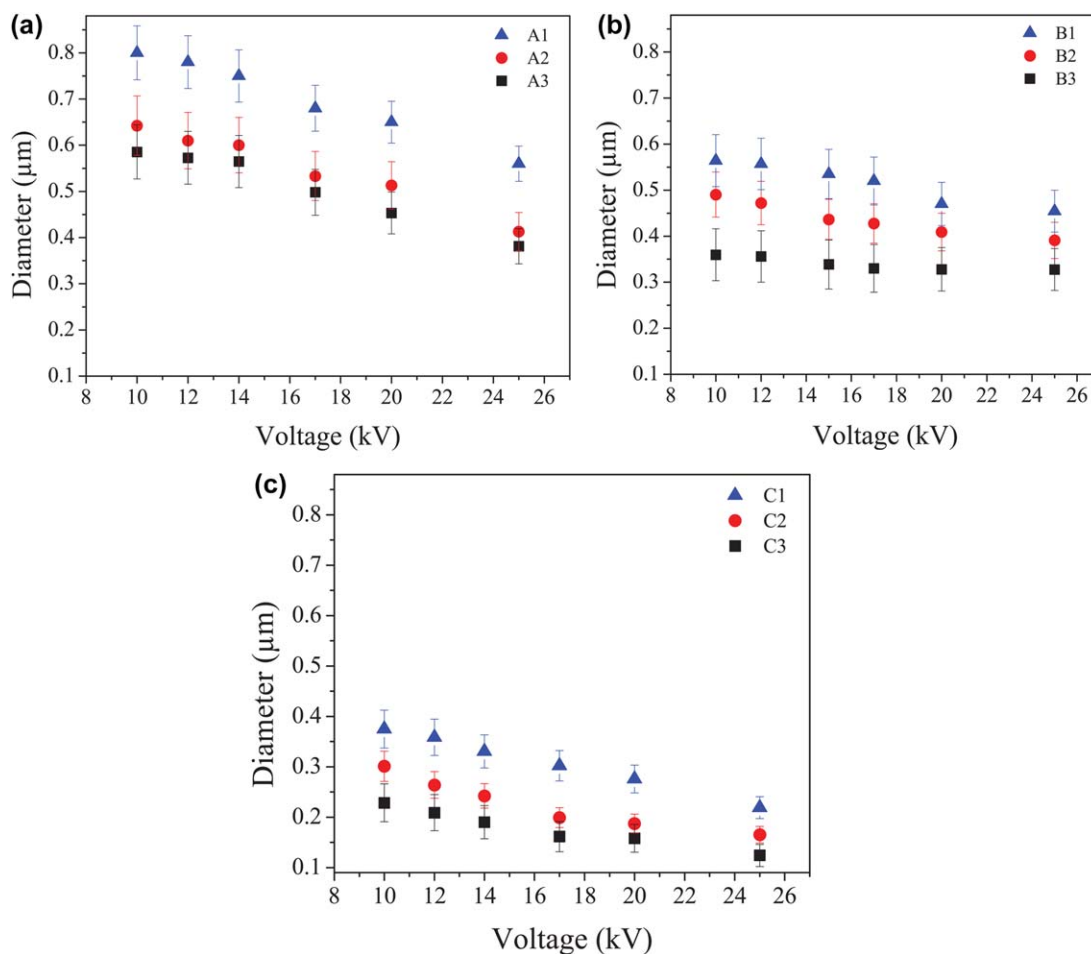
Figure 9. Effect of the applied voltage on the average diameter of electrospun fibers at flow rate of 10 mL h^{-1} for different precursors. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The literature findings regarding the effect of the applied voltage on the fiber diameter are controversial. Several groups suggested that higher voltages generate larger fiber.[30,31] Others suggested that higher voltages favor the narrowing of fiber diameter.[32] In addition, some groups also demonstrated that higher voltage offers the greater probability of beads formation.[33,34]

Our results presented in Figure 9 shows that increasing the voltage reduce the fibers diameter. Higher voltage causes greater stretching of the solution due to the greater Coulomb forces in the jet as well as a stronger electric field between the spinneret and the collector which lead to reduction in the fiber diameter.

No beads are formed in the range of used voltage for the nine precursors. Beaded structure is only obtained for low thickener LT30 concentration of 2%. Thus, voltage influences the fiber morphology and diameter, but the level of significance varies with the thickeners type and concentration in the precursor.

Figure 10 shows that the diameters are reduced by nearly half under the same parametric conditions when the thickener goes from A1 to B3 and from B3 to C3. The precursor A1 contains

13 g of the thickener LT 30, B3 contains 26 g of LT 15, and C3 contains 55 g of LT7.5. It points out that the same number of AAM monomer in the thickener but distributed among chains of different molecular weight (Figure 3) will not give the same fibers' diameter. Rather the lower the molecular weight of the thickener, the lower the fiber diameter.

As a summary, increasing the molecular weight of the thickener leads to thicker fibers. A wider range of diameters can be obtained when using higher molecular weight thickeners. This result is similar to other results found in literature on polymer solution and melts.[35] For a given precursor, thinner fibers are generated at lower thickener concentration as well at lower flow rate and higher voltage. By proper manipulation of these parameters fibers of desired diameter can be generated.

The ultimate goal is to achieve smaller scale dimensions without compromising the fibers electroactivity. Further studies should be undertaken to correlate the type of thickener used to the electroactive performance of the microfibers. The selection of optimal composition of the precursor should take in consideration not only the fibers diameter but also the hydrogel behavior.
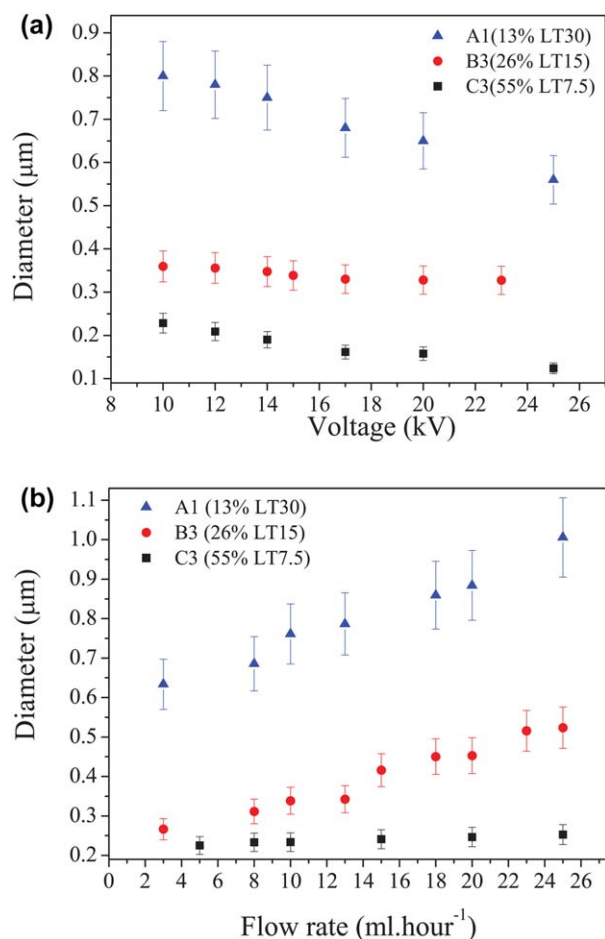
Figure 10. Effect of the: (a) applied voltage at flow rate of 10 mL h^{-1} and (b) flow rate voltage of 15 kV, on the average diameter of electrospun fibers for different precursors having the same quantity of AAM monomer in the thickener. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

The focus of this work is the processing of PAAM hydrogel material using electrospinning. The new presented setup and precursors form a modified process for the production of nano-fibers to microfibers via the electrostatic fiber spinning of polymer solutions. The main advantage of this technology is having a highly aligned electrospun fibers over large areas by a simple and low cost process.

The characteristics of the resultant fibers are highly dependent on the properties of the precursor and the processing parameters.

We should note that coupling the presented fabrication strategy with the appropriate choice of the precursor composition, microactuators possessing a wide range of mechanical properties may be produced.

The structural properties of fibers can be modified by adjusting the cross-linking degree (increasing the cross-linker concentration in the pre-gel solution); microfibers with improved mechanical property could be obtained.

Thus, by matching the fibers properties to *in vivo* demands, these fibers may have the potential to provide both a structural and functional mimic of the native tissue through intelligent biomaterial design.

Furthermore, the strategy followed for the fabrication could be further exploited to expand the repertoire of polymers that can be electrospun and to improve the arrangement of the deposited fibers.

REFERENCES

1. Teo, W. E.; Ramakrishna, S. *Nanotechnology* **2006**, *17*, 89.

2. Li, D.; Xia, Y. *Adv. Mater.* **2004**, *16*, 1151.

3. Bhardwaj, N.; Kundu, S. C. *Biotechnol. Adv.* **2010**, *28*, 325.

4. Quynh, P.; Pham, U. S.; Mikos, A. G. *Tissue Eng.* **2006**, *12*, 1197.

5. Kim, G.; Kim, W. *Appl. Phys. Lett.* **2006**, *88*, 233101.

6. Rafique, J.; Yu, J.; Yu, J.; Fang, G.; Wong, K. W.; Zheng, Z.; Ong, H. C.; Lau, W. M. *Appl. Phys. Lett.* **2007**, *91*, 063126.

7. Yang, D.; Lu, B.; Zhao, Y.; Jiang, X. *Adv. Mater.* **2007**, *19*, 3702.

8. Baji, A.; Mai, Y. W.; Wong, S.-C.; Abtahi, M.; Chen, P. *Compos. Sci. Technol.* **2010**, *70*, 703.

9. Huang, Z. M.; Zhang, Y. Z.; Kotaki, M.; Ramakrishna, S. *Compos. Sci. Technol.* **2003**, *63*, 2223.

10. De Santis, G.; Vinay, J.; Baccarani, A.; Pedone, A.; Pinelli, M.; Spaggiari, A.; Guaraldi, G. *Plast. Reconstructive Surgery* **2008**, *121*, 644.

11. Smith, E. A.; Oehme, F. W. *Rev. Environ. Health* **1991**, *9*, 215.

12. Bassil, M.; Ibrahim, M.; Habchi, R.; Davenas, J.; Boiteux, G.; El Tahchi, M. *J. Non-Cryst. Solids* **2010**, *356*, 754.

13. Bassil, M.; Davenas, J.; El Tahchi, M. *Sens. Actuators B* **2008**, *134*, 496.

14. Bassil, M.; El Tahchi, M.; Souaid, E.; Davenas, J.; Azzi, G.; Nabbout, R. *Smart Mater. Struct.* **2008**, *17*, 055017.

15. Bassil, M.; Davenas, J.; El Tahchi, M. *Adv.Sci. Technol.* **2008**, *61*, 85.

16. Bassil, M.; Ibrahim, M.; El Tahchi, M.; Farah, J.; Davenas, J. *MRS Proc.* **2009**, *1134*, 15.

17. Tanaka, T.; Fillmore, D. J. *J. Chem. Phys.* **1979**, *70*, 1214.

18. Gestos, A.; Whitten, P. G.; Wallace, G. G.; Spinks, G. M. *Soft Matter.* **2012**, *8*, 8082.

19. Shin, M. K.; Kim, S. I.; Kim, S. J.; Kim, S. K.; Lee, H.; Spinks, G. M. *Appl. Phys. Lett.* **2006**, *89*, 231929.

20. Beebe, D. J.; Moore, J. S.; Bauer, J. M.; Yu, Q.; Liu, R. H.; Devadoss, C.; Jo, B. H. *Nature* **2000**, *404*, 588.

21. Bassil, M.; Ibrahim, M.; El Tahchi, M. *Soft Matter.* **2011**, *7*, 4833.

22. Bottino, M. C.; Thomas, V.; Schmidt, G.; Vohra, Y. K.; Chu, T. M.; Kowolik, M. J.; Janowski, G. M. *Dental Mater.* **2012**, *28*, 703.

23. Pramani, K. S.; Pingguan-Murphy, B.; Osman, N. A. A. *Sci. Technol. Adv. Mater.* **2012**, *13*, 043002.

24. Pekcan, Ö.; Kara, S. *Polymer* **2001**, *42*, 7411.

25. Schultz, K. M.; Campo-Deaño, L.; Baldwin, A. D.; Kiick, K. L.; Clasen, C.; *Polymer* **2013**, *54*, 363.

26. Kara, S.; Okay, O.; Pekcan, Ö. *Polym. Bull.* **2000**, *45*, 281.

27. Kameoka, J.; Orth, R.; Yang, Y.; Czaplewski, D.; Mathers, R.; Coates, G. W.; Craighead, H. G. *Nanotechnology* **2003**, *14*, 1124.

28. Zong, X.; Kim, K.; Fang, D.; Ran, S.; Hsiao, B.S.; Chu, B. S. *Polymer* **2002**, *43*, 4403.

29. Megelski, S.; Stephens, J. S.; Chase, D. B.; Rabolt, J. F. *Macromolecules* **2002**, *35*, 8456.

30. Reneker, D. H.; Chun, I. *Nanotechnology* **1996**, *7*, 216.

31. Zhang, C.; Yuan, X.; Wu, L.; Han, Y.; Sheng, J. *Eur. Polym. J.* **2005**, *41*, 423.

32. Yuan, X.; Zhang, Y.; Dong, C.; Sheng, J. *Polym. Int.* **2004**, *53*, 1704.

33. Buchko, C. J.; Chen, L. C.; Shen, Y.; Martin, D. C. *Polymer* **1999**, *40*, 7397.

34. Demir, M. M.; Yilgor, I.; Yilgor, E.; Erman, B. *Polymer* **2002**, *43*, 3303.

35. Dasdemir, M.; Topalbekiroglu, M.; Demir, A. *J. Appl. Polym. Sci.* **2013**, *127*, 1901.