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SELF-ORGANIZATION OF FIBERS INTO YARNS DURING ELECTROSPINNING OF POLYCATION/POLYANION POLYELECTROLYTE PAIRS

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The self-organization of fibers into yarns during electrospinning of polycation/polyanion polyelectrolyte pairs is shown in the present contribution. This was achieved using 85 wt.% formic acid as a solvent in the presence of a low molecular weight salt ($CaCl_2$ or NaCl). Self-organization of the fibers into yarns without utilization of any supplementary appliances to the electrospinning apparatus was demonstrated for the pairs: (*i*) chitosan/poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS), and (*ii*) an ionene-type polycation/copolymer of AMPS and *t*-butyl acrylamide [P(AMPS-*co*-TBA)]. Yarns from chitosan/PAMPS with a diameter of ca. 300 μm were formed using a disk-type collector at rotating velocity of 100 rpm. In the case of the ionene-type polycation/P(AMPS-*co*-TBA) pair yarns were formed only in the presence of a low molecular weight salt. The diameter of the yarns depended on the salt concentration (from 0.25 mm to 0.90 mm at NaCl concentrations of 0.40 mol/L and 0.80 mol/L, respectively). The use of a rotating drum collector allowed producing a fluffy non-woven textile from the ionene-type polycation/P(AMPS-*co*-TBA) complex.

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1. Introduction

Polyelectrolytes are considered as a highly promising class of water-soluble polymers since they possess reactive functional groups. One of the most attractive features of these polymers is their ability to form water-insoluble polyelectrolyte complexes (PECs). The nano- and microfibrous materials consisting of PECs are of interest because they may find a wide range of applications. The electrospinning has been highlighted as one of the most promising techniques for fabrication of ultrathin fibers [1]. The preparation of fibers consisting of PECs by electrospinning using solutions that contain the oppositely charged polyelectrolyte partners has recently been reported [2,3]. Poly(acrylic acid) and poly(allylamine hydrochloride) [2], chitosan and poly(acrylic acid) [3], chitosan and PAMPS [3] have been used as polyelectrolyte partners. A main prerequisite for electrospinning of a solution containing oppositely charged polyelectrolytes is the selection of an appropriate solvent system that precludes the occurrence of phase separation due to PEC formation. For weak polyelectrolytes the solvent system has to be chosen as the pH value of the resulting solution to be beyond the pH-range in which the oppositely charged polyelectrolyte partners are able to form an insoluble PEC. Keeping the solution pH value of ca. 1, suitable electrospinning solutions from poly(acrylic acid)/poly (allylamine hydrochloride) and chitosan/poly(acrylic acid) pairs have been obtained [1,2]. Some of us have shown that when the

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strong polyacid PAMPS is used as an oppositely charged partner of chitosan, addition of a low molecular weight salt (e.g., $CaCl_2$) is required for preparation of a homogeneous spinning solution. The presence of a low molecular salt in the spinning solution alters the solution conductivity and the spinning jet motion, thus affecting the morphology of the electrospun materials and the fibers composing them. Recently, Wang et al. [4] have demonstrated that the presence of a low molecular weight organic salt (benzyl triethylammonium chloride) in spinning solutions of non-ionogenic polymers [poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), polyacrylonitrile, poly(L-lactic acid), and poly(*m*-phenylene isophthalamide)] can be used as an efficient tool for initiation of yarns formation during electrospinning without the use of supplementary appliances to the electrospinning apparatus. During the past few years the yarns materials obtained by electrospinning are regarded as new-generation textiles that can find diverse applications [5]. For polyelectrolytes the data on the preparation of yarns by electrospinning are still scarce. During the electrospinning of poly(*p*-xylenetetrahydrothiophenium chloride) alone a spontaneous process of self-organization of the fibers into yarns has been observed [6]. A similar phenomenon has been observed during the electrospinning of cellulose using its solution in dimethyl acetamide in the presence of LiCl [7]. To the best of our knowledge yarns formation during electrospinning of polyelectrolyte pairs able to form PECs has not been reported yet.

The aim of the present contribution is to demonstrate the possibility of self-organization of fibers into yarns by electrospinning of solutions of polycation/polyanion pairs using formic acid as a solvent. For that purpose two polyelectrolyte pairs have been selected: (*i*) chitosan and PAMPS, and (*ii*) an ionene-type polyelectrolyte and a copolymer of AMPS and *t*-butyl acrylamide [P(AMPS-*co*-TBA)].

2. Experimental

2.1. Materials

Chitosan (M_W 6×10^5 g/mol, deacetylation degree of 80% as determined by IR spectroscopy) and 2-acrylamido-2-methylpropanesulofnic acid (AMPS) were purchased from Fluka. PCA_5D_1 containing 94 mol % *N*,*N*-dimethyl-2-hydroxypropylammonium chloride units in the backbone and 1 mol % N-decyloxypropyl-2-hydroxypropyleneamine units was synthesized and purified as previously reported [8]. The intrinsic viscosity of PCA_5D_1 determined in 1 M NaCl at 25 ºC was $[\eta]_{1M\ NaCl}$ = 0.41 dL/g. The random copolymer of AMPS and *t*-butyl acrylamide P($AMPS_{0.37}$-*co*-$TBA_{0.63}$) with intrinsic viscosity of 0.47 dL/g (as determined in 1 M NaCl at 25º C) was synthesized according to a procedure described in details elsewhere [9] and is denoted as P(AMPS-*co*-TBA). PAMPS was synthesized by free radical polymerization as described elsewhere [10]. Its average molecular weight (1×10^6 g/mol) was determined by an Ubbelohde capillary type viscometer using known values of the Mark-Houwink constants [11]. Formic acid (85 wt.%), NaCl and $CaCl_2$ were purchased from Fluka.

2.2. Electrospinning of chitosan/PAMPS and PCA_5D_1/P(AMPS-*co*-TBA) pairs

The electrospinning set-up consisted of a syringe (5 mL) equipped with a needle with a conical nozzle. The needle was connected via an electrode to a high voltage power supply generating a positive DC voltage.

For the electrospinning of chitosan/PAMPS pair mixed solutions of chitosan and PAMPS in 85 wt.% HCOOH [H_2O/HCOOH = 1/6 (v/v)] in the presence of $CaCl_2$ (0.27 mol/L); total polymer concentration of 2.6 wt.% and [aminoglucoside units]/[AMPS-units] = 1/1 (mol/mol) were used. Briefly, 0.1 g PAMPS was dissolved in 3 mL HCOOH and 0.09 g $CaCl_2$ was added. Chitosan (0.09 g) was dissolved in 3 mL HCOOH and $CaCl_2$ (0.09 g) was added. A homogeneous and transparent solution was obtained after mixing of the initial polymer solutions (pH = 1). The spinning solution was delivered at a controlled feed rate of 1.1 $mL\cdot h^{-1}$ at a constant value of the applied voltage (38 kV). A vertical rotating disk-type collector with a diameter of 200 mm was

utilized as a collector. Its rotating velocity was varied from 0 to 100 rpm. The distance between the nozzle tip and the disk-type collector was 15 cm.

For the electrospinning of PCA_5D_1/P(AMPS-*co*-TBA) pair, a grounded stationary flat sheet or a rotating drum collector (at rotating velocity of 20 rpm) were used as collectors. The experiments were performed at total polymer concentration of 20 or 25 wt.%. The molar ratio between the charges of the polyelectrolyte partners was equal to 1/1. For total polymer concentration of 25 wt.%, 0.44 g (3 mmol) of PCA_5D_1 were dissolved in 3 mL of HCOOH, and 1.35 g (3 mmol) of P(AMPS-*co*-TBA) were dissolved in 3 mL of HCOOH. A homogeneous solution was obtained after mixing of the initial polymer solutions. For the experiments performed in the presence of a low molecular weight salt, NaCl was added after the complete homogenization of the solution. The solution was delivered at a controlled feed rate of 0.65 mL/h at a constant value of the applied voltage (30 kV), and at a constant distance between the nozzle tip and the collector (6 cm).

The electrical resistance of the spinning solutions was measured in an electrolytic cell equipped with rectangular sheet platinum electrodes having a surface area of 0.6 cm^2 and disposed at a distance of 2.0 cm. The solution resistance was measured with an accuracy of ± 3%. Calibration of the electrolytic cell was performed using standard KCl solutions and the cell constant (K_{cell}) was determined. The conductivity of the solutions (σ, μS/cm) was calculated from the following equation:

$$\sigma = \frac{1}{\rho} = \frac{1}{K_{cell}.R} \tag{1}$$

where ρ is the specific resistance of the solution (μΩ·cm), R - electrical resistance of the solution (μΩ).

2.3. Characterization of the fibrous materials

The morphology of the electrospun fibrous materials was evaluated by means of scanning electron microscopy (SEM). For this purpose the non-woven textiles were vacuum-coated with carbon and gold, and analyzed using a SEM Philips 515 or JEOL JSM-5010. The fiber morphology was studied in terms of the criteria for complex evaluation of electrospun materials reported in details elsewhere [12] using Image J software [13] by measuring at least 20 fibers from each SEM image. To determine the stability of PEC nanofibers in aqueous medium, the yarn materials were immersed in deionized water for 24 h. The treated samples were freeze-dried, and then observed by SEM.

3. Results and discussion

The preparation of PEC-based fibrous textiles by electrospinning is of interest because of the opportunity for design of functional materials that can find diverse applications. Their hydrogel behavior in contact with aqueous solutions can be tuned by the polyelectrolyte partners' nature (weak or strong polyelectrolytes) and medium conditions (pH and ionic strength values). The preparation of yarns from PECs by electrospinning broadens the applicability of fibrous materials based on polyelectrolytes. Having in mind the shown by Wang et al. [4] self-organization of fibers into yarns induced by the presence of a low molecular weight salt during electrospinning, in the present contribution the possibility to prepare yarns from chitosan/PAMPS pair in the presence of $CaCl_2$ was evaluated. For that purpose 85 wt.% HCOOH was used as a solvent because of its ability in the presence of the low molecular weight salt to preclude PEC formation [3]. Furthermore, in the present study the applicability of 85 wt.% HCOOH as a suitable solvent for another polyelectrolyte pair and the peculiarities of the yarns formation from this pair were examined as well.

3.1. Self-organization during electrospinning of chitosan/PAMPS solutions

The strong polyacid PAMPS forms complexes with the weak polybase chitosan which are stable in a relatively broad pH-range [10]. The prepared PECs are biocompatible materials [14]. As aforementioned, in formic acid a homogeneous solution containing both chitosan and PAMPS can be formed only in the presence of a low molecular weight salt [3]. Growing of a significant number of individual fibrous bundles in direction from the collector to the nozzle tip was observed during the electrospinning of chitosan/PAMPS/$CaCl_2$ when using a stationary disk-type collector (Figure 1).

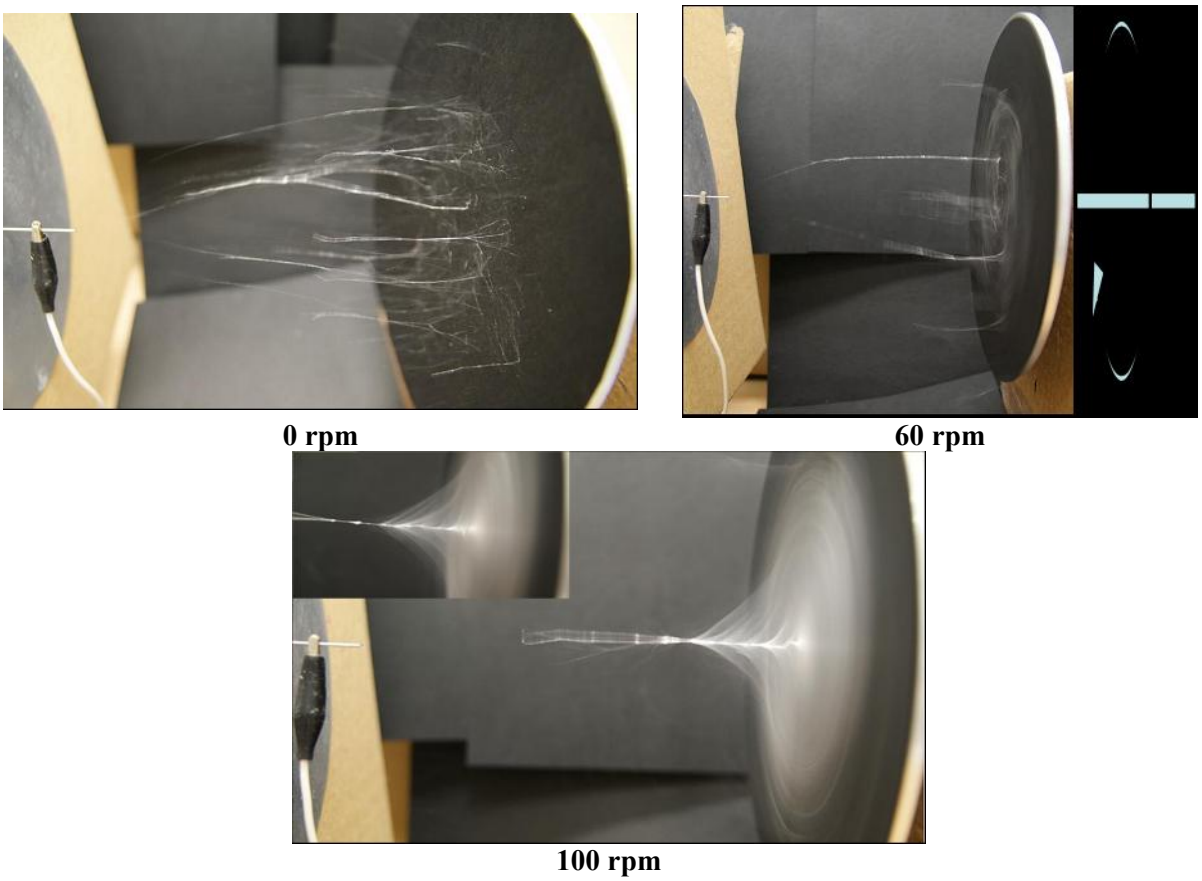
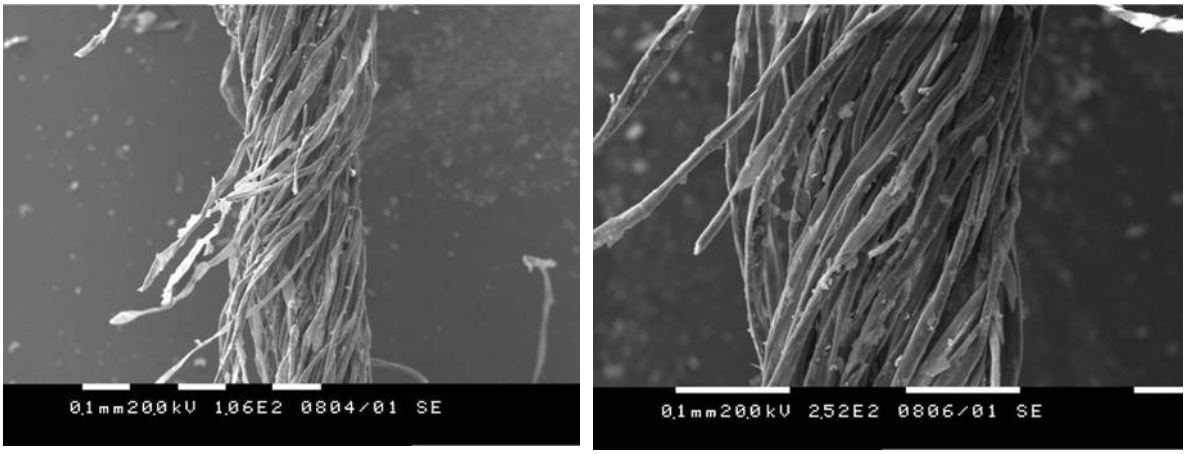


Fig. 1. Photographs of spontaneous yarn formation from fibers prepared by electrospinning of chitosan/PAMPS/$CaCl_2$ solutions onto a rotating disk-type collector at a rotating velocity of 0; 60 or 100 rpm; total polymer concentration: 2.6 wt.%, 0.27 mol/L $CaCl_2$.

The initially formed bundles tended to thicken. At rotating velocity of 60 rpm a similar self-organization in numerous individual bundles was observed. Organization of the fibers into a yarn occurred at higher rotating velocity. Most probably at higher rotating velocity the time period is insufficient for the fibers to organize into separate bundles. SEM micrographs of the yarn obtained in the gap between the collector and the nozzle tip at rotating velocity of 100 rpm are shown in Figure 2. The diameter of the obtained yarn is ca. 300 μm, and the mean diameter of the fibers composing it is 1000 ± 200 nm. Breakage of some of the fibers was observed at rotating velocity of 100 rpm and was attributed to the strain at twisting into a yarn.



A **B**

Fig. 2. SEM micrographs of a fibrous yarn obtained in the gap between the nozzle tip and the rotating disk-type collector at rotating velocity of 100 rpm during electrospinning of chitosan/PAMPS/$CaCl_2$ solutions; total polymer concentration: 2.6 wt.%; $CaCl_2$ concentration: 0.27 mol/L. Magnification: ×100 (A) and ×250 (B).

3.2. Self-organization during the electrospinning of PCA_5D_1/P(AMPS-*co*-TBA) solutions

In aqueous solutions the strong polyelectrolytes PCA_5D_1 and P(AMPS-*co*-TBA) (Figure 3) form insoluble PECs in the whole pH-range. Interestingly enough, it was found that in formic acid their mixed solutions are homogeneous, without any addition of a low molecular weight electrolyte. This was attributed to the presence of hydrophobic units in P(AMPS-*co*-TBA) and in PCA_5D_1.

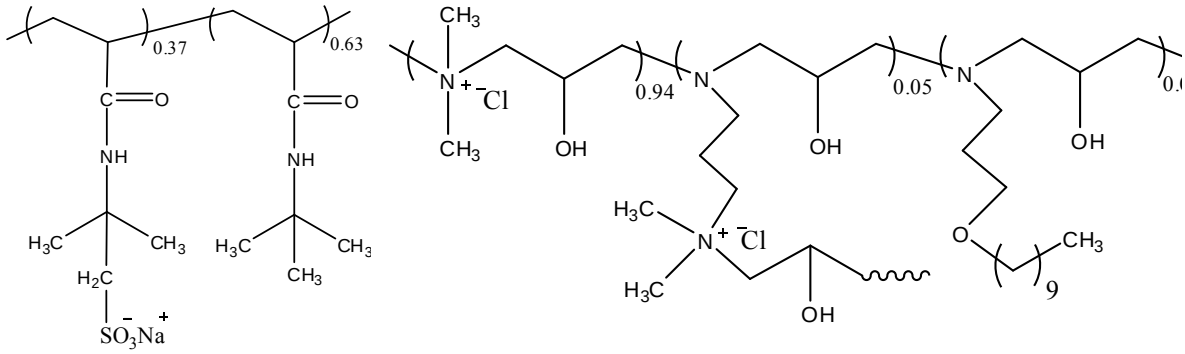
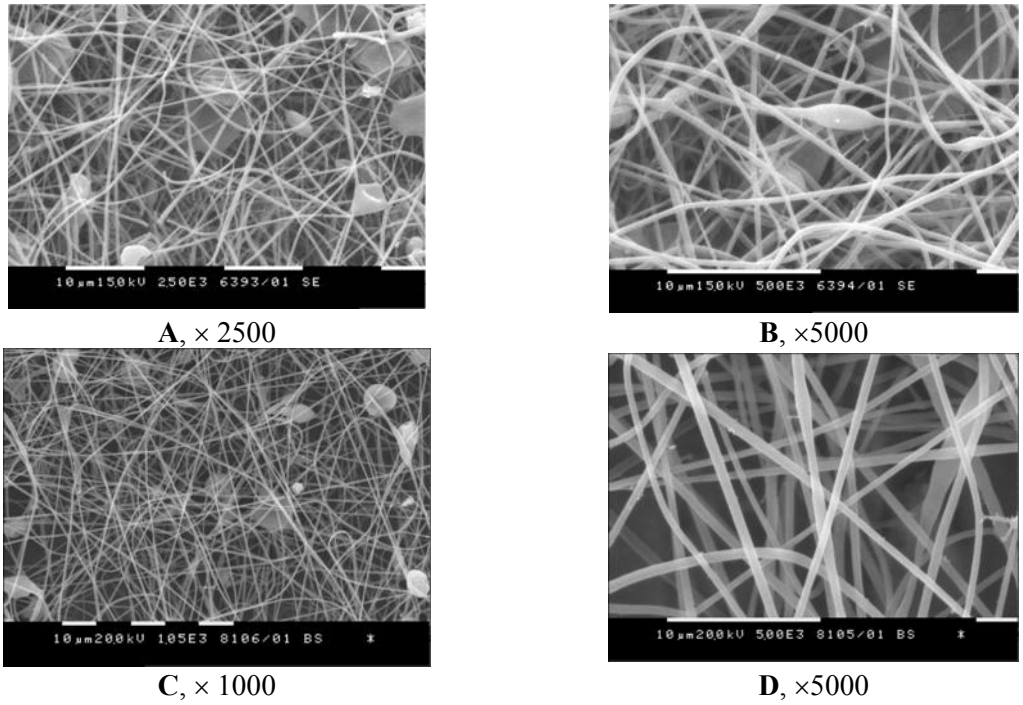


Fig. 3. Fragments of PCA_5D_1 and P(AMPS-co-TBA) structures.

This assumption was supported by the finding that when PAMPS was used as a partner instead of the P(AMPS-*co*-TBA) copolymer, phase separation occurred in the absence of a low molecular weight salt. SEM micrographs of fibrous mats prepared from solutions of PCA_5D_1/P(AMPS-*co*-TBA) pair in 85 wt.% HCOOH at total polymer concentration of 20 wt.% or 25 wt.% in absence of a low molecular weight salt are shown in Fig. 4.



A, × 2500 **B**, ×5000

C, × 1000 **D**, ×5000

Fig. 4. SEM micrographs of nanofibers prepared by electrospinning of PCA_5D_1/P(AMPS-co-TBA) solutions using 85 wt.% HCOOH as a solvent; total polymer concentration: 20 wt.% (A and B); 25 wt.% (C and D).

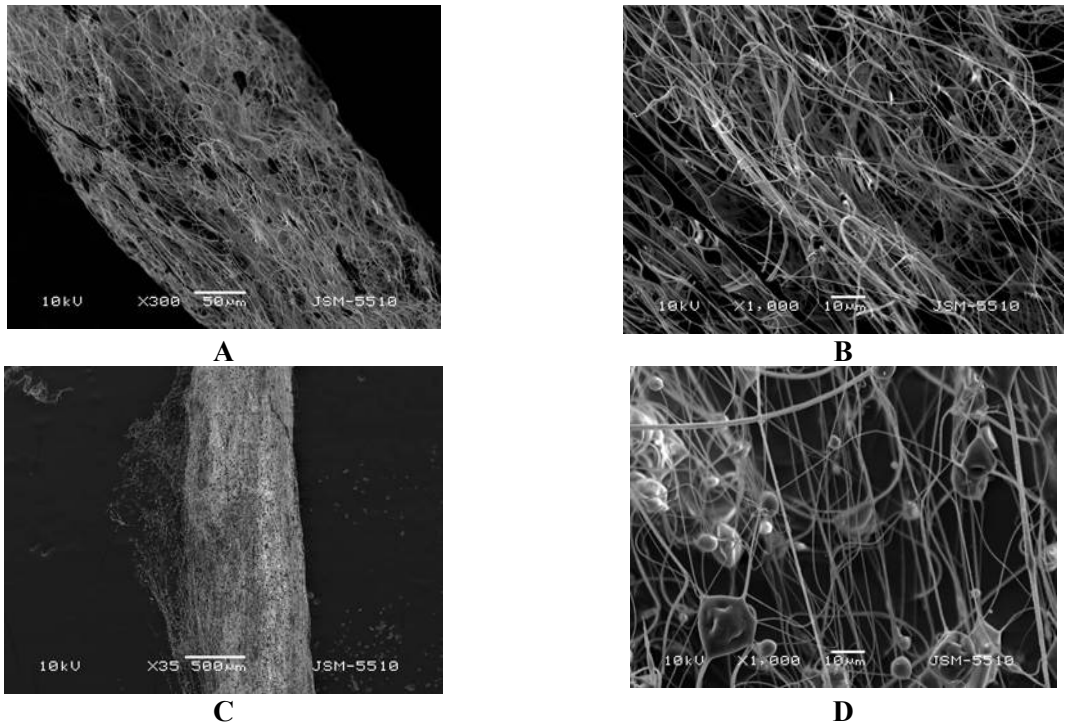
Mats consisting of randomly deposited fibers were obtained under these conditions. At total polymer concentration of 20 wt.%, some spindle-like defects were formed along the fibers (Figure 4A and B). The determined mean diameter of their defect-free section was 380 ± 124 nm. The increase of the polymer concentration to 25 wt.% resulted in producing fibers with few defects (Figure 4C and D). However, the fiber diameter was almost twice as large (600 ± 140 nm) most probably because of the higher solution viscosity. It is worth to be noted that the spinning solution conductivity was as high as 5500 µS/cm. The high conductivity is due to the polyelectrolyte nature of the polymer partners. Despite the high conductivity self-organization of the fibers into yarns was not observed, and the electrospinning of the solutions led to random deposition of the fibers onto the collector.

Having in mind that chitosan/PAMPS solution from which yarns formation was observed contains a low molecular weight salt, in a next series of experiments the effect of the addition of NaCl into PCA_5D_1/P(AMPS-*co*-TBA) solutions on the self-organization ability was examined. The content of NaCl was adjusted to be 0.40 mol/L or 0.80 mol/L. Formation of yarns growing in direction from the collector to the nozzle tip was observed during the electrospinning of PCA_5D_1/P(AMPS-*co*-TBA) solutions in the presence of NaCl (Figure 5).

t = 5 min **t = 15 min**

Fig. 5. Photographs of spontaneous formation of yarns from fibers prepared by electrospinning of solutions from PCA_5D_1/P(AMPS-co-TBA) containing 0.40 mol/L NaCl, electrospinning time: 5 or 15 min; total polymer concentration: 25 wt.%.

In the presence of 0.40 mol/L NaCl the solution conductivity value increased up to 8460 μS/cm. The electrospinning of PCA_5D_1/P(AMPS-*co*-TBA) solution in the presence of 0.40 mol/L NaCl led to the formation of yarns with a diameter of ca. 0.25 mm (Figure 6 A and B).



A **B**

C **D**

Fig. 6. SEM micrographs of yarns prepared by electrospinning of PCA_5D_1/P(AMPS-co-TBA) in the presence of NaCl at concentration: 0.40 mol/L (A and B) and 0.80 mol/L (C and D); total polymer concentration: 25 wt.%; the samples were taken after 40 min electrospinning.

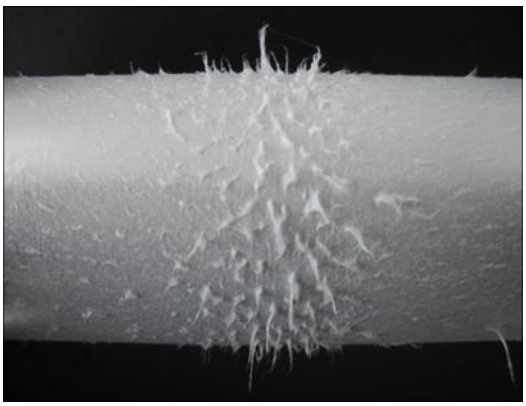
The determined mean diameter of the fibers which compose the yarn was 570 ± 135 nm. The increase of NaCl concentration up to 0.80 mol/L led to fabrication of yarns having larger diameters (ca. 0.90 mm). At 0.80 mol/L NaCl the fibers composing the yarns had some defects along their axis and the mean diameter of their defect-free section was 440 ± 172 nm (Figure 6 D).

The larger yarns diameter and the presence of defects along the fibers are attributed to the higher solution conductivity (9720 μS/cm) as compared to that at NaCl concentration of 0.40 mol/L.

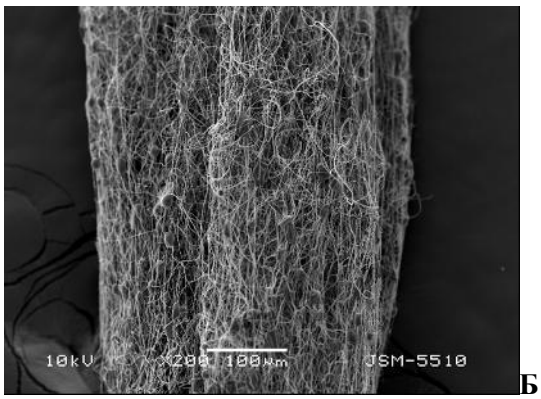
Samples of PCA_5D_1/P(AMPS-*co*-TBA) fibrous material were immersed for 24 h in deionized water. The fibrous mat structure was retained thus evidencing the formation of PEC. The performed SEM analyses of such samples after freeze-drying revealed that the fibers were ribbon-like shaped with a mean width of 2000 ± 300 nm (Figure 7). The change in the shape and the size of the fibers is due to swelling of the PEC-based fibers.

Fig. 7. SEM micrographs of PCA_5D_1/P(AMPS-co-TBA) fibers prepared by electrospinning in the presence of 0.80 mol/L NaCl after a 24 h stay in deionized water followed by freeze-drying.

When the electrospinning was performed using a rotating drum collector, it was possible to obtain a fluffy material (Figure 8A).



А



Б

Fig. 8. A photograph (A) and a SEM micrograph (B) of a fluffy textile prepared by electrospinning of PCA_5D_1/P(AMPS-co-TBA) solutions, total polymer concentration: 25 wt.%, in the presence of 0.40 mol/L NaCl using a rotating drum collector at rotating velocity of 20 rpm.

The obtained peculiar structures of the surface of the textile formed were due to self-organization of the fibers in yarns. These structures differed in terms of length and diameter values. The yarns were conical in shape in their bottom part; their upper section had a shape close to the cylindrical one. The SEM micrograph presented in Figure 8B was recorded using a sample taken from the upper section of a yarn having a length of ca. 5 mm. The yarn diameter is ca. 0.38 mm and the mean diameter of its constituting fibers is 500 ± 150 nm.

4. Conclusions

Self-organization of fibers from polycation/polyanion pairs into yarns was achieved by electrospinning. The presence of a low molecular weight salt in the spinning solutions is considered as the main prerequisite for initiation of the self-organization process. The morphology of the obtained materials depends on the composition of the spinning solution (polymer nature and low molecular weight electrolyte concentration), as well as on the collector type. The obtained results demonstrate the feasibility of diverse in terms of morphology fibrous electrospun mats which may allow broadening the range of application of these PEC-based materials.

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References

[1] D. Paneva, M. Ignatova, N. Manolova, I. Rashkov, Novel chitosan–containing micro- and nanofibrous materials by electrospinning: preparation and biomedical application, in: W. N. Chang (Ed.), Nanofibers: Fabrication, Performance, and Applications, Nova Science Publishers, Inc., pp. 73-151 (2009).
[2] A. Chunder, S. Sarkar, Y. Yu, L. Zhai, Coll. Surf. B: Biointerf. **58**, 172 (2007).
[3] H. Penchev, D. Paneva, N. Manolova, I. Rashkov, Macromol. Rapid Commun. **29**, 677 (2008).
[4] X. Wang, K. Zhang, M. Zhu, H. Yu, Z. Zhou, Y. Chen, B.S. Hsiao, Polymer **49**, 2755 (2008).
[5] F.-L. Zhou, R.-H. Gong, Polym. Int. **57**, 837 (2008).
[6] H. Okuzaki, T. Takahashi, N. Miyajima, Y. Suzuki, T. Kuwabara, Macromolecules **39**, 4276 (2006).
[7] A. Frenot, M.W. Henriksson, P. Walkenström, J. Appl. Polym. Sci. **103**, 1473 (2007).
[8] S. Dragan, L. Ghimini, Angew. Makromol. Chem. **192**, 199 (1991).
[9] E.S. Dragan, M. Mihai, S. Schwarz, Colloids Surf. A **290**, 213 (2006).
[10] O. Stoilova, N. Koseva, N. Manolova, I. Rashkov, Polym. Bull. **43**, 67 (1999).
[11] L.W. Fisher, A.R. Sochor, J.S. Tan, Macromolecules **10**, 949 (1977).
[12] M. Spasova, R. Mincheva, D. Paneva, N. Manolova, I. Rashkov, J. Bioact. Compat. Polym. **21**, 465 (2006).
[13] W.S. Rasband, ImageJ, U. S. National Institute of Health, Bethesda, Maryland, USA, http://rsb.info.nih.gov/ij/ (1997-2006).
[14] D. Paneva, N. Manolova, I. Rashkov, D. Danchev, J. Bioact. Compat. Polym. **20**, 133 (2005).