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Effect of Solution Concentration on the Electrospray/Electrospinning Transition and on the Crystalline Phase of PVDF

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ABSTRACT

A study was conducted regarding the effect of concentration of poly (vinylidene fluoride) (PVDF)/N,N-dimethylformamide (DMF) and PVDF/DMF/acetone solutions on the transition between electrospray and electrospinning and on the formation of the α and β crystalline phases of PVDF. The crystalline phases present in the samples, crystallinity and morphology were determined by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM), respectively. Low concentration solutions resulted in films consisting of small droplets (electrospray) containing predominantly the β phase. High concentration solutions resulted in a non-woven mesh of nano-to-micron diameter fibers (electrospinning) containing exclusively the β phase. These results showed that, the formation of this phase in the electrospinning is related mainly to the solvent evaporation rate, and not to drawing experienced by the polymer during the process. Solvent type affected the amount of crystalline phase present, the boundary concentration between the two processes and the average diameter of fibers. Meshes processed by electrospinning display a degree of crystallinity higher than the films obtained by electrospray.

1. Introduction

PVDF, poly(vinylidene fluoride), is a widely investigated polymer due to its excellent mechanical properties, chemical stability and ferroelectricity. This polymer has a simple chemical formula, $-CH_2-CF_2-$, and may crystallize in at least four crystalline phases known as α, β, γ and δ. The structure and property of these phases are well documented in the literature [1]. Each crystalline phase confers characteristic properties to the polymer and therefore distinct applications. The β phase is that which displays the strongest pyro and piezoelectric activities and is therefore technologically more interesting. Many techniques have been used to obtain this phase, being the most common uni or biaxial drawing of originally α phase films [2-6]. Crystallization of PVDF from solution (casting) may also result in the β phase, depending on the evaporation rate of the solvent [7-9]. Low rates result predominantly in the β phase, whereas high rates favor the α phase. Electrospinning [10,11] also produces pre-

dominantly the β phase [12-18]. In this technique the polymer solution is added to a capillary (which can be a syringe with needle). The solution forms a droplet at the tip of the needle due to surface tension. If a sufficiently high electric voltage (5-30 kV) is applied to the solution electric charges accumulate in the droplet. When the electrostatic repulsion between the charges overcomes the surface tension and viscoelasticity of the droplet this assumes the shape of a cone. When the force exerted by the electric field, formed between the droplet and a grounded collector, overcomes the surface tension, a thin jet is formed. The jet of the charged solution is accelerated towards the collector under the action of the electric field. If the concentration of the solution is sufficiently high (viscous) to stabilize the jet, the polymer solution is severely stretched and the solvent evaporates to form ultrathin fibers which solidify and are deposited on the collector forming a non-woven mesh of fibers. Some authors [13-17] attribute the formation of β phase in electrospun PVDF meshes to this severe drawing ex-

perienced by the polymer jet solution. This elongation process would be similar to the well known $\alpha \rightarrow \beta$ transition caused by mechanical drawing at $T < 90°C$ [2-6].

A variant of electrospinning is electrospray [19]. The basic difference between these two processes lies in the concentration of the solution. In electrospray the concentration is sufficiently low to destabilize the charged jet which then breaks down into small spherical droplets that solidify during the course and are deposited on the collector. In this case the polymer solution does not experience severe drawing and the formed film consists of small droplets instead of fibers.

The objectives of the current investigation were: 1) determine the solution concentration at which the transition between electrospray and electrospinning of PVDF occurs and 2) verify through the electrospray technique, where no stretching occurs, that the formation of the β phase depends fundamentally on the solvent evaporation rate. The effect of the type of solvent in the process was also verified.

2. Experimental Methods

2.1. Materials

The PVDF used was Foraflon® 4000HD, from Elf Atochem. The solvents used were N,N-dimethylformamide (DMF, Merck 99.5%) and acetone (Merck, 99.7%). Solutions were prepared at concentrations of 5, 7, 10 and 15 wt% PVDF using as solvent pure DMF and a 3:1 v/v mixture of DMF with acetone. The ratio of mixture DMF and acetone was selected because they produce thinner and more homogeneous nanofibers in the electrospinning process [13]. Solubilization was carried out at 70°C under stirring for one hour. **Table 1** shows some properties of the solvents used.

2.2. Electrospray/Electrospinning

A scheme of the system used in the electrospray/electrospinning process is shown in **Figure 1**. A 20-mL glass syringe was used with a steel needle with internal diameter of 0.7 mm. The distance between needle and collector was 3 cm and the electric voltage applied was 10 kV, using a Bertan 210 30R (0-30 kV) high voltage source. The collector used was an aluminum disk with diameter of 15 cm and width of 5 cm, at an angular velocity of 60 rpm. The process was carried out at 25°C and RH ≈ 55%.

2.3. Characterizations

The crystalline phases present in the samples were characterized by transmission infrared spectroscopy (FTIR, Perkin Elmer Spectrum 1000) in the range between 400 and 1000 cm⁻¹ and with resolution of 2 cm⁻¹. Calorimetric analyses were conducted in a Perkin Elmer DSC-7, cali-

Table 1. Properties of the solvents used (20°C).

Solvent	Formula	Density (g/mL)	Boiling point (°C)	Viscosity (mPa.s)
Acetone	C_3H_6O	0.786	56.5	0.326
DMF	C_3H_7NO	0.944	153	0.820

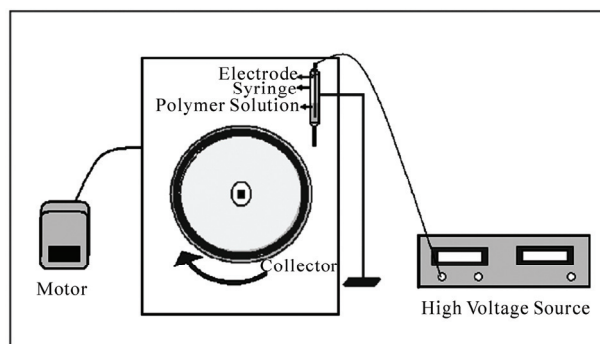**Figure 1. Scheme of the setup used in the Electrospinning/ Electrospray process.**

brated with In, using samples of ~8 mg and heating rate of 10°C/min. Degree of crystallinity was determined by comparing the enthalpy of fusion of the sample obtained by DSC with that of 100% crystalline PVDF-α (104.5 J/g) [20]. Sample surface morphology was observed by using a scanning electron microscope (Philips 30 FEG Model XL, operating at 15 kV) after gold coating. Size distribution of the fibers diameters was determined by the software "image J" developed by the National Institute of Health.

3. Results and Discussions

The micrographs in **Figures 2(a)** to **(d)** and **3(a)** to **(d)** present the morphology of the samples processed with PVDF/DMF and PVDF/DMF/acetone solutions at different concentrations, respectively.

One can observe in **Figures 2(a)-(b)** (5 and 7 wt% in DMF) and **3(a)** (5 wt% in DMF/acetone) the formation of a film consisting of small droplets, characteristic of the electrospray process. The morphology of this film depends among other things on droplet volume at impact and on evaporation rate of the solvent [21]. In **Figures 2(c)-(d)** (10, 15 wt% in DMF) and **3(b)-(d)** (7, 10 and 15 wt% in DMF/acetone) fibers predominate, characteristic of electrospinning. In micrographs **2(c)** (10 wt% in DMF) and **3(b)** (7 wt% in DMF/acetone) the electrospun sheets present some small droplets, demonstrating that concentration was not yet ideal for the formation of homogeneous fibers. These results show that the boundary concentration between electrospray and electrospinning ranges from 7 to10 wt% PVDF in DMF and from 5 to 7 wt% in
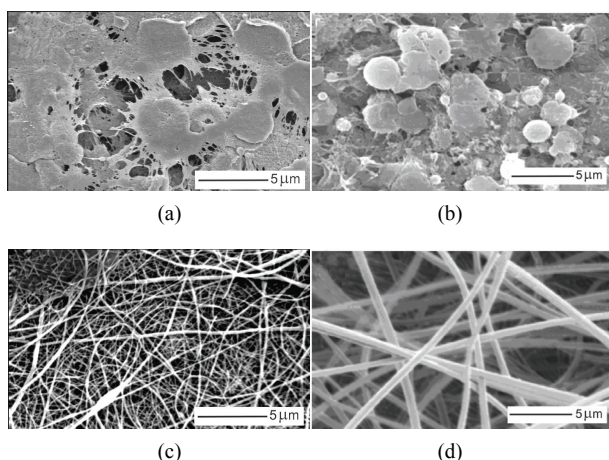
Figure 2. Micrographs of the samples processed from PVDF/ DMF solution at the following concentrations (wt%): (a) 5; (b) 7; (c) 10 and (d) 15.
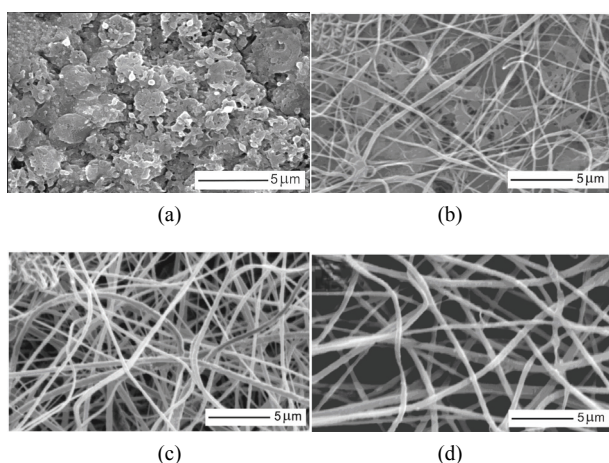

Figure 3. Micrographs of samples processed from solution of PVDF with DMF/acetone (3:1 v/v) at the following concentrations (wt%): (a) 5; (b) 7; (c) 10 and (d) 15.

DMF/acetone mixture, at the conditions used of voltage and distance between needle and collector. The solution containing acetone is less viscous than that of pure DMF and therefore the electrospinning process should be initiated at a higher concentration. However, the high volatility of acetone increased the jet concentration rapidly during its course towards the collector, impeding formation of droplets and resulting in electrospinning at a lower initial concentration. Micrographs **2(d)** (15 wt% in DMF) and **3(c)-(d)** (10 and 15 wt% in DMF/acetone) show fibers with improved homogeneity and no droplets, indicating that these concentrations are the optimum for obtaining electrospun meshes.

   Figures 4 and **5** contain the size distribution of fibers diameters prepared with 15 wt% PVDF in DMF and DMF/acetone, respectively.
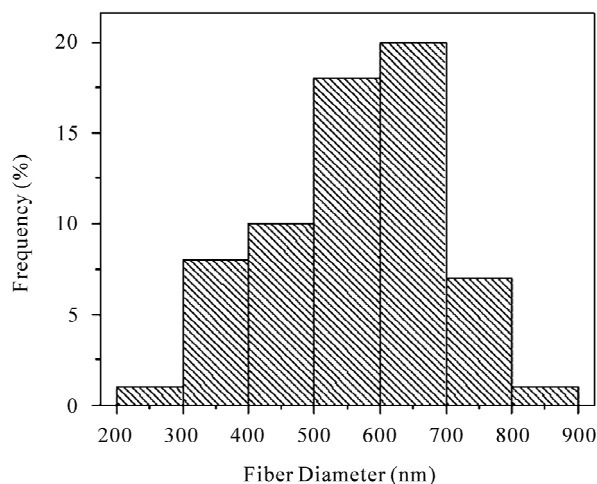

Figure 4. Size distribution of the fibers diameters processed from 15 wt% PVDF/DMF solution.
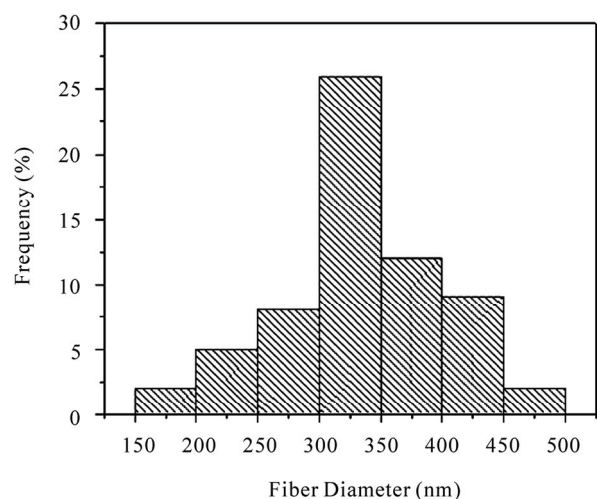

Figure 5. Size distribution of the fibers diameters processed from 15 wt% PVDF/DMF/acetone.

   Average diameter of the nanofibers prepared from DMF solution (514 nm) were superior to that obtained from DMF/acetone solution (330 nm), at the same concentration. This has been caused by the lower viscosity of the acetone solution, since average fiber diameter increases with solution viscosity [12]. That effect can be observed in **Figures 2(c)-(d)** and **3(b)-(d)**.

   The phases present in the samples were analyzed by FTIR and results are presented in **Figures 6** and **7** for DMF and DMF/acetone solutions at different concentrations, respectively.

   All samples presented bands at 445, 510 and 840 cm^{-1}, characteristic of the β phase of PVDF [22,23]. Therefore, the β phase predominated both in the electrosprayed films and the electrospun meshes. Since no stretching occurred during electrospray, we may conclude that for
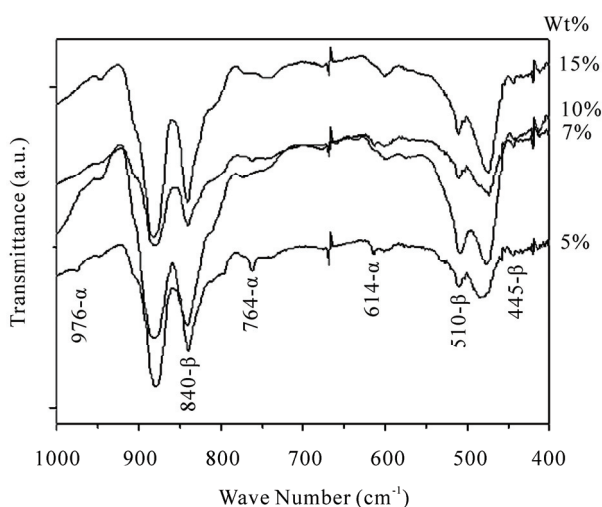
Figure 6. FTIR spectra of the samples with different wt% PVDF in DMF solution. The characteristic bands of the α and β phase are pointed out in the figure.
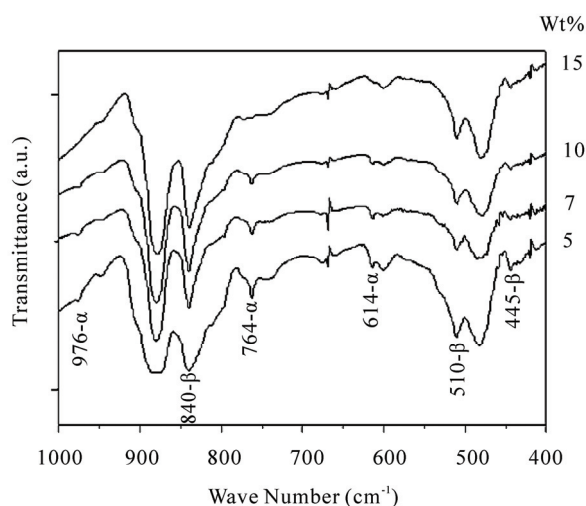

Figure 7. FTIR spectra of the samples with different wt% PVDF in 3:1 DMF/acetone solution. The characteristic bands of the α and β phase are pointed out in the figure.

mation of this phase can not be attributed to drawing experienced by the polymer during the process. The occurrence of weak bands at 614, 764 and 976 cm^{-1} indicate the presence of a small amount of the α phase [22,23], observed at concentrations of 5 to 10 wt% in DMF/acetone solution. In the solution containing pure DMF the presence of the α phase was only observed for 5 wt%. Since solvent evaporation rate increases with decreasing concentration of the solution, appearance of this phase may be related to the higher solvent evaporation rate in low-concentration solutions. The evaporation rate of the solutions containing acetone increased in relation to those containing pure DMF, since acetone has a lower evapo-

ration temperature, and this resulted in the formation of a small amount of α in almost all concentrations. Thus, the formation of the β phase in the electrospinning/electrospray process is related mainly to the solvent evaporation rate, as verified in cast films [8,9], and not to drawing experienced by the polymer during the electro-spinning process, as suggested by some authors [13-17]. Low evaporation rates result predominantly in the β phase, thermodynamically more favorable, intermediate rates in a mixture of α and β and high rates in the α phase, kinetically more favorable.

Figure 8 shows DSC curves for samples prepared with 5 and 10 wt% PVDF in DMF and DMF/acetone. The DSC measurements give the melting point (T_m) (endotherm peak), enthalpy of fusion (ΔH), and degree of crystallinity (%C) of samples. These values are summarized in **Table 2**.

It is easy to observe that meshes produced by electrospinning display a degree of crystallinity higher when compared to films obtained by electrospray. This result probably happens due to the preferential orientation of the chains in the direction of the nanofibers, caused by the drawing experienced by the polymer during the electrospinning and that facilitates the crystallization. In this process the addition of acetone promoted a small increase in the degree of the mesh crystallinity. The melting points, in all cases correspond to the temperature range related to the PVDF α and β phases [7,23], which confirm FTIR results.

4. Conclusions

The current investigation showed that formation of the β crystalline phase of PVDF in the electrospun meshes is
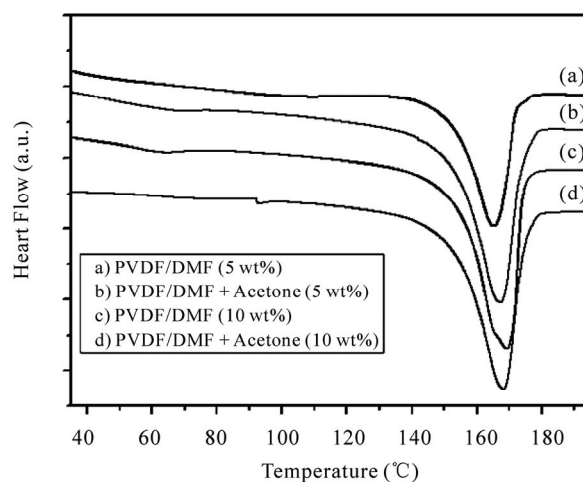

Figure 8. DSC curves for samples prepared with 5 wt% PVDF in DMF (a) and DMF/acetone (b); with 10 wt% PVDF in DMF (c) and DMF/acetone (d).

Table 2. Melting point (T_m), enthalpy of fusion (ΔH) and degree of cristallinity ($\%C$) of the samples processed with PVDF/DMF and PVDF/DMF/acetone solutions at different concentrations.

Sample	Process	T_m (℃)	ΔH (J/g)	$\%C$
5 wt% PVDF/DMF	Electrospray	166	46.2	44.6
5 wt% PVDF/DMF/acetone		167	46.8	45.2
10 wt% PVDF/DMF	Electrospinning	168	53.4	51.1
10 wt% PVDF/DMF/acetone		167	55.0	53.1

not related to drawing experienced by the polymer during the process, as suggested by some authors. Formation of the α and β phase is related primarily to the evaporation rate of the solvent. High rates favor formation of the α phase, whereas low rates favor the β phase. Under the same conditions of voltage and needle-collector distance, the boundary concentration between electrospray and electrospinning depends on the solvent used. For PVDF this concentration lies between 7 and 10 wt% with DMF as solvent and between 5 and 7 wt% for the 3:1 DMF/acetone mixture. Moreover, addition of acetone to the solution reduced average fiber diameter. Meshes produced by electrospinning present degree of crystallinity higher than the films obtained by electrospray, for both used solvents.

5. Acknowledgements

REFERENCES

[1]   K. Tashiro, "Crystal Structure and Phase Transition of PVDF and Related Copolymers," In: H. S. Nalwa, Ed., *Ferroelectric Polymers*: *Chemistry, Physics and Applicaons*, Marcel Dekker, New York, 1995, pp. 63-180.

[2]   R. Gregorio, Jr. and E. M. Ueno, "Effect of Crystalline Phase, Orientation and Temperature on the Dielectric Properties of Poly(Vinylidene Fluoride) (PVDF)," *Journal of Materials Science*, Vol. 34, 1999, pp. 4489-4500.

[3]   V. Sencadas, V. M. Moreira, S. Lanceros-Mendez, A. S. Pouzada and R. Gregorio, Jr., "Alpha-to-Beta Transformation on PVDF Films Obtained by Uniaxial Stretch," *Advanced Materials Forum III*, Vol. 514-516, 2006, 872-876.

[4]   P. Sajkiewicz, A. Wasiak and Z. Goclowski, "Phase Transitions during Stretching of Poly(Vinylidene Fluoride)," *European Polymer Journal*, Vol. 35, No. 3, pp. 423-429.

[5]   D. T. Grubb and F. R. Kearney, "Phase Transitions during Stretching of Poly(Vinylidene Fluoride)," *Journal of Polymer Science Part B*: *Polymer Physics*, Vol. 28, No. 11, 1990, pp. 2071-2078.

[6]   M. C. Branciforti, V. Sencadas, S. Lanceros-Mendez and R. Gregorio, Jr., "New Technique of Processing Highly Oriented Poly(Vinylidene Fluoride) Films Exclusively in the β Phase," *Journal of Polymer Science Part B*: *Polymer Physics*, Vol. 45, 2007, pp. 2793-2801.

[7]   R. Gregorio, Jr., and M. Cestari, "Effect of Crystallization Temperature on the Crystalline Phase Content and Morphology of Poly(Vinylidene Fluoride)," *Journal of Polymer Science Part B*: *Polymer Physics*, Vol. 32, No. 5, pp. 859-870.

[8]   R. Gregorio, Jr. and D. S. Borges, "Effect of Crystallization Rate on the Formation of the Polymorphs of Solution Cast Poly(Vinylidene Fluoride)," *Polymer*, Vol. 49, No. 18, 2008, pp. 4009-4016.

[9]   D. L. Chinaglia, R. Gregorio, Jr., J. C. Stefanello, R. A. P. Altafin, W. Wirges, F. Wang and R. Gerhard, "Influence of the Solvent Evaporation Rate on the Crystalline Phases of Solution-Cast Poly(Vinylidene Fluoride) Films," *Journal of Applied Polymer Science*, Vol. 116, No. 2, 2010, pp. 785-791.

[10] A. Formhals, "Process and Apparatus for Preparing Artificial Threads," U.S. Patent 1,975,504, 1934.

[11] J. Doshi and D. H. Reneker, "Electrospinning Process and Application of Electrospun Fibers," *Journal of Electrostatics*, Vol. 35, No. 2-3, 1995, pp. 151-160.

[12] M. Nasir, H. Matsumoto, T. Danno, M. Minagawa, T. Irisawa, M. Shioya and A. Tanioka, "Control of Diameter, Morphology, and Structure of PVDF Nanofiber Fabricated by Electrospray Deposition," *Journal of Polymer Science Part B*: *Polymer Physics*, Vol. 44, No. 5, pp. 779-786.

[13] W. A. Yee, M. Kotaki, Y. Liu and X. Lu, "Morphology, Polymorphism Behavior and Molecular Orientation of Electrospun Poly(Vinylidene Fluoride) Fibers," *Polymer*, Vol. 48, No. 2, 2007, pp. 512-521.

[14] E. Ogut, O. S. Yordem, Y. Z. Menceloglu and M. Papila, "Poly(Vinylidene Fluoride)/Zinc Oxid Smart Composite Material," *Proceeding of SPIE*, Vol. 6526, 2007, p. 65260Q-1-10

[15] J. Zheng, A. He, J. Li and C. C. Han, "Polymorphism Control of Poly(Vinylidene Fluoride) through Electrospinning," *Macromolecular Rapid Communications*, Vol. 28, No. 22, 2007, pp. 2159-2162.

[16] W. A. Yee, A. C. Nguyen, P. S. Lee, M. Kotaki, Y. Liu, B. T. Tan, S. Mhaisalkar and X. Lu, "Stress-Induced Structural Changes in Electrospun Polyvinylidene Difluoride Nanofibers Colleted Using a Modified Rotating Disk," *Polymer*, Vol. 49, No. 19, 2008, pp. 4196-4203.

[17] J. S. Andrew and D. R. Clarke, "Effect of Electrospin-ning on the Ferroelectric Phase Content of Polyvinylidene Difluoride Fibers," *Langmuir*, Vol. 24, No. 3, 2008, pp. 670-672.

[18] H. Na, Y. Zhao, C. Zhao, C. Zhao and X. Yuan, (2008) Effect of Hot-Press on Electrospun Poly(Vinylidene Fluo-ride) Membranes," *Polymer Engineering and Science*, Vol. 48, No. 5, pp. 934-940.

[19] G. Taylor, "Electrospray," *Proceedings of Royal Society of London*, *London*, Vol. A280, 1964, pp. 383-387.

[20] K. Nakagawa and Y. Ishida, "Dielectric Relaxations and Molecular Motions in Poly(Vinylidene Fluoride) with Crystal Form II," *Journal of Polymer Science Part B*:

Polymer Physics, Vol. 11, No. 8, pp. 1503-1533.

[21] I. B. Rietveld, K. Kobayashi, H. Yamada and K. Matsu-shige, "Model Supported Morphology Control of Elec-trospray Deposited Poly(Vinylidene Fluoride) Film," *Macromolecular Symposium*, 2007, pp. 249-250, 322-329.

[22] M. Kobayashi, K. Tashiro and H. Tadokoro, "Molecular Vibrations of Three Crystal Forms of Poly(Vilidene Fluo-ride)," *Macromolecules*, Vol. 8, No. 2, 1975, pp. 158-170.

[23] R. Gregorio, Jr., "Determination of the α, β and γ Crys-talline Phases of Poly(Vinylidene Fluoride) Films Pre-pared at Different Conditions," *Journal of Applied Poly-mer Science*, Vol. 100, No. 4, 2006, pp. 3272-3279.