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Preparation of Fully Hydrolyzed Ultra-High-Molecular-Weight Polyvinyl Alcohol Nanofibers by Viscosity Control and Improvement of Fiber Hot Water Resistance by Annealing

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Abstract：Fully hydrolyzed ultra-high-molecular-weight polyvinyl alcohol (PVA) electrospun fibers with uniform diameters of about 200 nm were fabricated by reducing the viscosity of PVA in aqueous solution. A novel viscosity-modifier (hydrazine monochloride, HMC) gradually reduces the viscosity of PVA aqueous solution over a period of several days. This phenomenon is counter to the usual effect of ionic salt addition. After being stored for several days, the viscosity decreased by up to 60 % compared to that of an equivalent pure PVA solution. Using HMC to control the viscosity of the PVA solution made it possible to fabricate ultrafine electrospun fibers. In addition, the hot water resistance of the fibers was obviously improved by annealing.

1. Introduction

Electrospinning is an inexpensive and relatively simple method to produce fibers with diameters in the nanometer range [1-5]. Polyvinyl alcohol (PVA) is one of the most popular polymers used for ultrafine electrospun fiber production. Nano-scale PVA fibers have several interesting characteristics, such as high surface area to mass ratio, significant possibilities for surface functionalization, and high mechanical performance due to an improvement in the molecular organization of the spun fiber. These properties make electrospun PVA fibers excellent candidates for many applications, such as filtration, reinforcing materials, wound dressings and drug releasing carriers [6-11].

Fully hydrolyzed ultra-high-molecular-weight PVA (FH-UHMW-PVA), with a degree of polymerization (DP) $\geq$ 8000, can be used to produce "super fibers" with high strength and high modulus due to the intrinsically high chemical stability, water resistance, and excellent physical and mechanical properties of the parent material. FH-UHMW-PVA nanofibers would therefore also have better properties than those produced from ordinary PVA. However, electrospinning nanofibers from FH-UHMW-PVA is extremely difficult due to the extremely high viscosity in solution, even at low concentrations [12-15], and the use FH-UHMW-PVA to fabricate ultra fine electrospun fibers has not yet been reported.

We have however, successfully fabricated electrospun FH-UHMW-PVA fibers with nominal diameters of 200 nm by controlling the solution viscosity. Hydrazine monochloride (HMC) is widely used in organic synthesis, but until now has not been used for reducing the viscosity of PVA [16]. The effect of HMC on the viscosity characteristics of the solutions was investigated and a reason for the change is proposed. Furthermore, parameters such as concentration and storage time were systematically examined and their effects on the morphology and diameter of electrospun FH-UHMW-PVA fibers are described. In addition, the solubility of the fibers, as shown by resistance to hot water was improved by annealing. It is now possible to produce ultrafine FH-UHMW-PVA electrospun fibers with excellent hot water resistance.
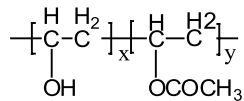
2. Experimental

2.1 Materials

Samples of PVA with a degree of hydrolysis (DH) > 99 % and a degree of polymerization (DP) = 8000, and with DH > 99 % and DP = 1700 were kindly provided by Kuraray Co. Ltd, Tokyo, Japan. In this paper the abbreviation form, PVA-X-Y, is adopted to characterize polymer molecular weight and degree of hydrolysis. For example, PVA-80-99 represents a PVA with a DP of 8000 and a DH of 99 %. As we known, PVA is produced industrially by hydrolysis of poly(vinyl acetate). Thus, DH of PVA is simply defined as the following :

$$DH = \frac{x}{x+y} \times 100\%$$

where x and y are the molar fractions of the hydroxyl and the acetate groups, respectively, specified in the following stoichiometric formula :

$$\left[\begin{matrix} H & H_2 \\ C-C \\ | \\ OH \end{matrix}\right]_x \left[\begin{matrix} H & H_2 \\ C-C \\ | \\ OCOCH_3 \end{matrix}\right]_y$$

Hydrazine monochloride (HMC, or $N_2H_4 \cdot HCl$) and isopropanol (IPA) were obtained from Tokyo Chemical Industry Co., Ltd. All chemicals were of analytical grade and were used without further purification. De-ionized (DI) water was used as the solvent.

2.2　Preparation of PVA solutions

PVA-80-99 aqueous solution was prepared using the method described by Briscoe et al [17]. In brief, PVA powder was dispersed in distilled water at 25 °C for 2 h and this suspension was rapidly heated to above 95 °C and kept at this temperature with high speed stirring for about 3 h. The solution was then cooled to room temperature. Various amounts of HMC were added to certain amounts of PVA solution to make solutions with HMC concentrations of 0.05 mol/L, 0.1 mol/L and 0.3 mol/L. These solutions were stirred for 2 hours to ensure homogenization and then put into a 40 °C water bath for several days. Viscosity, conductivity and surface tension were measured every 24 h at a temperature of 25 °C.

2.3　Electrospinning

The electrospinning experiments were performed at 25 °C. The polymer solution was placed in a 12 mL syringe with a 0.8 mm id needle, and the needle was connected to the high voltage power supply. A rotating cylinder wrapped with aluminum foil was used as a grounded collector. The applied voltage and the tip-to-collector distance (TCD) were fixed at 10 kV and 15 cm. The syringe pump flow rate was set to 0.3 mL/h. Immediately before electrospinning, isopropanol (IPA) was added at 5 wt% to the PVA solutions to slightly modify the surface tension [18].

2.4　Annealing and water resistance

Immediately after spinning, the electrospun fibers were dried at room temperature in a vacuum oven for 2 h. Then annealing treatment was proceeded at 180 °C for 2 h. The samples remained under vacuum for further 2 h to cool down before being removed from the oven. The annealed PVA fibers were immersed in DI water at 25 °C, 40 °C and 60 °C for 3 days separately. The samples were then transferred into isopropyl alcohol for 5 min before loading in a chamber to complete the drying process under vacuum (0.002 MPa) for later SEM charac-terization.

2.5　Measurement

The rheological properties of the PVA-80-99 solutions were measured using a Rheologia-A300 controlled stress rheometer (ELQUEST) at 25 °C. A co-axial cylinder arrangement with a gap of 2.1 mm was used to measure the apparent viscosities using the Steady Flow Viscosity Testing mode. Samples were tested after various storage times and a recycling-water bath was employed to ensure constant temperature surroundings. Apparent viscosities of different PVA solutions measured at a shear rate of 100 1/sec were selected as reference viscosities.

Molecular weight measurements were performed on the Zetasizer Nano series (Malvern Instruments, UK) using a process called Static Light Scattering (SLS). All PVA solutions were tested under a series of concentrations under 0.1 wt%. The molecular weight was calculated through the modified Rayleigh equation [19] as follows :

$$\frac{KC}{R_\theta} = \frac{1}{M} + 2A_2C \tag{1}$$

R_θ : The Rayleigh ratio.

M : Sample molecular weight.

A_2 : 2nd Virial Coefficient.

C : Concentration.

The conductivity of the solutions was measured using a conductivity meter (Model SC72 personal SC meter, Yokogawa Electric Corporation), and a tension meter (CBVP-Z, Kyowa Interface Science Co. Ltd, Saitama, Japan) using the Wilhelm plate method, was used to determine surface tension. The morphology of electrospun fibers was observed on a scanning electron microscope (SEM, Hitachi S-3000N) on samples sputtered with Palladium-Platinum.

Table 1 Molecular weight of PVA (SLS data)

Concentration of HMC	PVA molecular weight ($\times 10^3$)			
	0	0.05 M	0.1 M	0.3 M
As-prepared	786	755	540	499
After 168 h	795	742	533	503

3. Results and discussion

3.1　Effect of Molecular weight on the viscosity of PVA

PVA-80-99 is nearly completely hydrolyzed, and so a preparation temperature above 95 °C is required for the complete dissolution of the solid in an acceptable time. It is believed that both the inter- and intra-molecule hydrogen bonding in aqueous PVA solutions is disrupted

by thermal energy during solution, but upon cooling the hydrogen bonds can re-form resulting in an increase in viscosity [20-22].

The viscosity of a PVA solution (η) depends on the molecular weight (M_w), concentration (c), degree of hydrolysis and the type of solvent. The dependence of zero shear viscosity on Mw in many polymers can be described by the Mark[Houwink equation :

$$[\eta] = K(M_w)^a$$

where "K" and "a" are the Mark-Houwink constants. Generally, the effects of Mw and c on solution viscosity can be modeled [23,24] as :

$$\eta = K(c\rho)^{\alpha}(M_w)^{\beta}$$

(α is empirical single-parameter and ρ is solution density) According to the equation, the viscosity of the solution depends strongly on M_w and concentration. Furthermore, for fully hydrolyzed PVA aqueous solutions, there is inter- and intra chain hydrogen bonding between the polar hydroxyl groups in the PVA molecules, which will lead to a more rapid increase in viscosity. As shown in Fig. 1, the viscosity of a 6 wt% PVA-17-99 solution is only 0.3 Pa·s, but the viscosity of PVA-80-99 is about 2 Pa·s, and the rate of increase of viscosity accelerates in proportion to concentration.
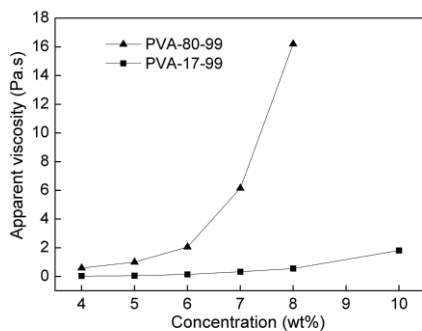

Fig. 1 The change in apparent viscosity of PVA aqueous solutions with molecular weight and concentration at 25 °C (Shear rate : 100 1/sec).

3.2 Effect of HMC on the viscosity of PVA

Aqueous solutions of fully hydrolyzed PVA undergo a viscosity increase with time and may finally gel. It is reported that several additives, such as inorganic salts and organic compounds (Na_2SO_4, NaCl and KCl) will increase the viscosity, and a few such as NH_4SCN and IPA have a distinct viscosity stabilizing effect [25]. However, we find that HMC has an unexpected effect on the viscosity of aqueous PVA, as can be seen in Fig. 2, where in the presence of HMC, the apparent viscosity of PVA in solution decreases gradually with storage time with final

viscosities reduced by up to 60 % depending on the amount of HMC. The addition of HMC may disrupt PVA chain inter- and intra-chain hydrogen bonding resulting in a decrease viscosity.
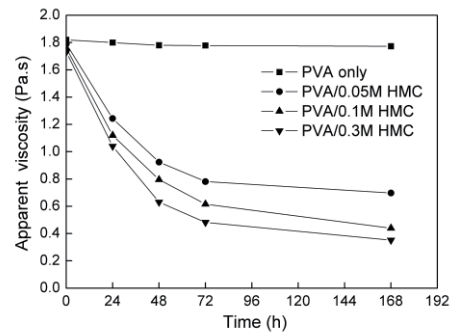
Fig. 2 The variation of apparent viscosity of FH-UHMW-PVA aqueous solutions with varying amounts of HMC at 25 °C (Shear rate : 100 1/sec).

Fig. 3 shows the relationship between shear rate and apparent viscosity for different PVA solutions after 168 h. Clear shear thinning behavior is observed in the pure PVA-80-99 solution. This is due the ultra high molecular weight (causing more entanglements between the PVA chains) and the higher DH (causing more inter and intra chain hydrogen bonding in the solution) and hence a high degree of interaction between the PVA chains. This shear thinning behavior also indicates the presence of stronger polymer chain associations. In addition, after the viscosities had decreased, the PVA-80-99 solutions show almost no shear thinning. According to the SLS data as shown in Table 1, the molecular weights of our samples have almost no change although their viscosities greatly decreased. It is probable that the addition of HMC reduces inter- and intra-chain hydrogen bonding and thus reduces the degree of interaction and entanglement between the molecular chains in PVA-80-99.
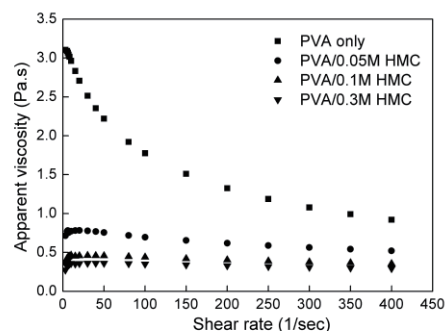
Fig. 3 Relationship between apparent viscosity and shear rate for PVA aqueous solutions with varying concentrations of HMC at 25 °C (storage time : 168 h).

3.3 Electrical conductivity and surface tension

We have also examined electrical conductivity and surface tension, which are important factors in electrospinning [26]. As seen in Fig. 3, the surface tension was slightly reduced by adding HMC while the conductivities increased sharply in proportion with the concentration of HMC. However, both the surface tension and conductivity changed very little during the period of storage although during the same period the viscosity decreased greatly.

(a)   (b)
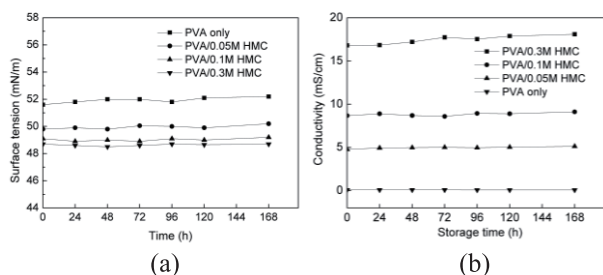
Fig. 4 Surface tension (a) and conductivity (b) of PVA in aqueous solution with different concentrations of HMC and varying storage time at 25 °C.

3.4 Electrospinnability

The fundamental processes in electrospinning are related to solution viscosity and surface tension ; these properties also significantly affect the morphology and diameter of the fibers [27-31]. It is very different to fabricate electrospun fibers using FH-UHMW-PVA because of the extremely high solution viscosity, even at low concentration : viscosity is the critical factor in electrospinning of FH-UHMW-PVA.

We proposed the use of a special additive, HMC, to reduce the viscosity of PVA-80-99 solutions and thence to electrospin fibers. Electrospun PVA-80-99 fibers fabricated from solutions with different viscosities, controlled by a combination of HMC addition and aging are shown in Fig. 5. From the pure PVA control solution (Fig. 5a), long threads with irregular thick structures were formed from the high surface tension and viscosity precursor solutions. However, in the presence of HMC, the diameters of electrospun fibers are significantly decreased (when the concentration of HMC is above 0.3 M and after 168 h) and fibers with diameter of 200-250 nm could be fabricated. This is a combined effect due to the decrease of surface tension and the increase in conductivity, and the decrease in viscosity. Control of all these factors is required to get regular morphology ultrafine fibers.

To reveal the relationship between viscosity, fiber diameter and morphology, PVA-80-99 solution with
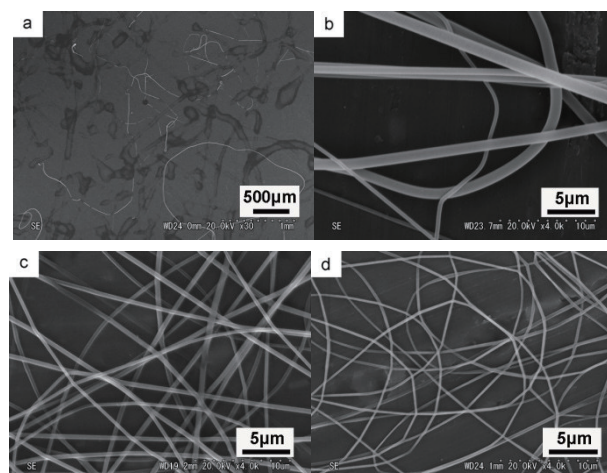
Fig. 5 SEM images of electrospun PVA-80-99 fibers produced from different solutions : (a) PVA only ; (b) PVA/0.05 M HMC ; (c) PVA/0.1 M HMC ; (d) PVA/0.3 M HMC). (Storage time : 168 h)

0.3 M HMC was selected as a model solution since its surface tension and conductivity remained virtually constant (shown in Fig. 6), even as the viscosity gradually decreased during the storage period : electrospun fibers from this solution are shown in Fig. 6. Initially, both the conductivity and viscosity are high and it is difficult to form a stable jet and only some spotty deposition was observed on the aluminum foil target (Fig. 6a). After
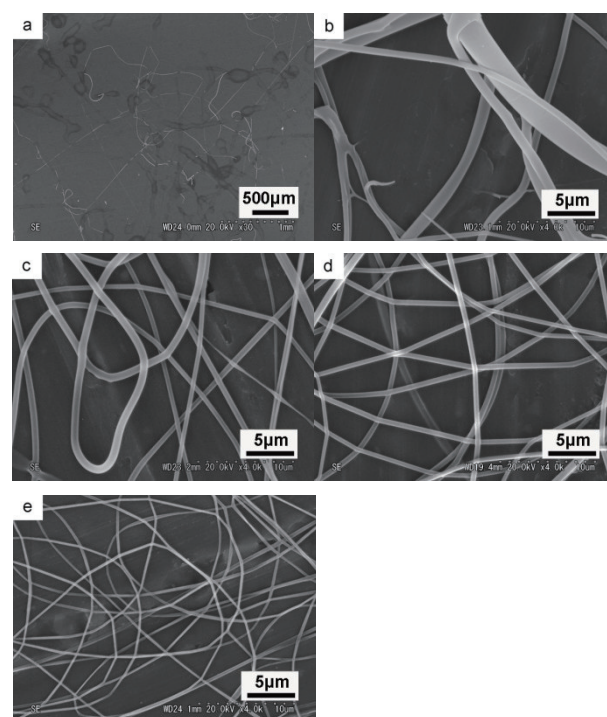
Fig. 6 SEM images of PVA-80-99 nanofibers produced from solutions containing 0.3 M HMC at various storage times : (a) Immediately after preparation ; (b) 24 h storage ; (c) 72 h storage ; (d) 120 h storage ; (e) 168 h storage.

several days of storage, the solution viscosity decreased, and uniform electrospun fibers could be fabricated. All the results indicate that viscosity is a predominant factor affecting fiber diameter. Electrospun PVA-80-99 fibers with diameter down to about 200 nm can be fabricated by this method of controlling viscosity.

3.5 Stabilization of PVA fibers against dissolution

The biggest drawback of electrospun PVA nanofibers, and a significant limit to their practical application, is the poor stability in water of the material [32,33]. When an electrospun PVA mat is immersed in water, the mat instantaneously shrinks and the unique nanofibrous structure is lost by dissolution into the aqueous environment. As shown in Fig. 6, the as-spun PVA-17-99 fibers display very poor stability in water (the left side of SEM image of Fig. 7a). After immersion in DI water for 1 min, the fiber structure has completely disappeared and a film with no porosity has formed. However, if ultra high molecular PVA, PVA-80-99 is subjected to the same treatment, the fiber structure still can be seen
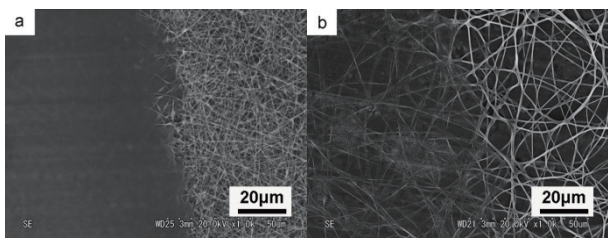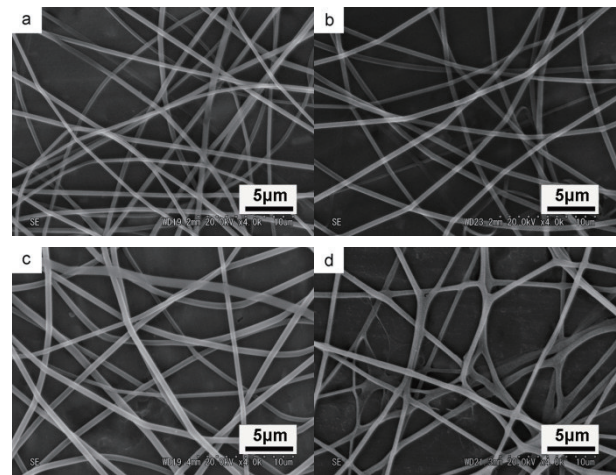

Fig. 7 SEM images of PVA fibers after immersed in 25 °C DI water for 1 min (a) PVA-17-99 ; (b) PVA-80-99

To improve the water resistance of PVA nanofibers, most researchers have concentrated on chemical cross-linking by a variety of substances including glutaraldehyde, acetaldehyde, or formaldehyde [34,35]. The process of annealing is an alternative physical treatment to increase the stability of PVA nanofibers [36]. Electrospun PVA-80-99 nanofibers were annealed at 180 °C in a nitrogen atmosphere. This treatment improves the stability of the PVA-80-99 nanofibers, and also has the beneficial effect of eliminating any vestige of HMC that might still be present. The treated fibers were immersed in water at different temperatures for several days to test the water resistance. As seen in Fig. 8, after 3 days, there was almost no change for samples immersed at temperatures up to 40 °C, and even at 60 °C there is still a significant fibrous character (Fig. 8d).

It is believed that annealing increases the degree of crystallinity, and hence the number of physical cross-links

in electrospun PVA fibers. This may occur by removal of bound water within the fibers allowing PVA-water hydrogen bonding to be replaced by intermolecular polymer hydrogen bonding and also increasing the degree of crystallization.

Fig. 8 SEM images of PVA-80-99 fibers with 2 h of 180 °C annealing treatment after (a) annealing ; (b) immersed in 25 °C DI water for 3 days ; (c) immersed in 40 °C DI water for 3 days ; (d) immersed in 60 °C DI water for 3 days.

4. Conclusion

We present the novel use of HMC to reduce the viscosity of fully hydrolyzed UHMW PVA. The viscosity of PVA-80-99 in aqueous solution is decreased gradually with time in proportion to the amount of HMC present ; this is opposite to the effect of the addition of ionic salts. After 7 days of storage, the viscosities of PVA-80-99 solutions had decreased by about 60 % (related to the concentration of HMC) compared to those of the original solutions. These phenomena are related to the reconfiguration of hydrogen bonding in the solutions. The morphology of PVA-80-99 electrospun fibers produced from solutions with different viscosities were investigated by SEM, and it was observed that the electrospun fibers became more uniform and the diameters became smaller as the concentration of HMC or the storage time increased. As a result, the spinnability of fully hydrolyzed UHMW PVA can be significantly improved by using this method, making it possible to readily produce ultrafine fully hydrolyzed UHMW PVA electrospun fibers with diameters about 200 nanometers. Furthermore, by simple annealing treatment, the electrospun fibers can remains their structure even in 60 °C water.

References

1. S. H. Tan, R. Inai, M. Kotaki, S. Ramakrishna, *Polymer*, **46**, 6128 (2005).

2. K. H. Lee, O. Ohsawa, S. Lee, J. C. Park, K. W. Kim, H. Y. Kim, Y. Watanabe, I. S. Kim, *Sen'i Gakkaishi*, **64**, 306 (2008).

3. J. H. Park, B. S. Kim, Y. C. Yoo, M. S. Khil, H. Y. Kim, *J. Appl. Polym. Sci.*, **107**, 2211 (2007).

4. J. Doshi, D. H. Reneker, *J. Electrostat.*, **35**, 151 (1995).

5. K. Wei, T. Ohta, B. S. Kim, K. H. Lee, M. S. Khil, H. Y. Kim, I. S. Kim, *Polym. Adv.Technol.*, **21**, 746 (2010).

6. J. M. Deitzel, J. Kleinmeyer, D. Harris, N. C. Beck Tan, *Polymer*, **42**, 261 (2001).

7. C. Chen, Y. H. Zhu, H. Bao, X. L. Yang, C. Z. Li, Appl. Mate. Interfaces, **2**, 1499 (2010).

8. B. E. B. Jensen, A. A. A. Smith, B. Fejerskov, A. Postma, P. Senn, E. Reimhult, M. Pla-Roca, L. Isa, D. S. Sutherland, B. Stadler, A. N. Zelikin, *Langmuir*, **27**, 10216 (2011).

9. A. D. Ossipov, J. Hilborn, *Macromolecules*, **39**, 1709 (2006).

10. D. A. Ossipov, S. Piskounova, J. Hilborn, *Macromolecules,* **41**, 3971 (2008).

11. F. Cavalieri, E. Chiessi, R. Villa, L. Vigano, N. Zaffaroni, M. F. Telling, G. Paradossi, *Biomacromolecules*, **9**, 1967 (2008).

12. S. I. Song, B. C. Kim, *Polymer*, **45**, 2381 (2004).

13. A. Koski, K. Yim, S. Shivkumar, *Mater. Lett*., **58**, 493 (2004).

14. W. S. Lyoo, S. J. Lee, J. H. Kim, S. K. Noh, B. C. Ji, B. C. Kim, *J. Appl. Polym. Sci.,* **93**, 41 (2004).

15. H. M. Ji, H. W. Lee, M. R. Karim, I. W. Cheong, E. A. Bae, T. H. Kim, M. S. Islam, B. C. Ji, J. H. Yeum, *Collo. Polym. Sci.,* **287**, 751 (2009).

16. W. W. Wang, Y. J. Zhu, M. L. Ruan, *J. Nanopart. Res.*, **9**, 419 (2007).

17. B. Briscoe, P. Luckham, S. Zhu, *Polymer*, **41**, 3851 (2000).

18. A. Saluja, A. V. Badkar, D. L. Zeng, S. Nema and D. S. Kalonia, *Biophysical Journal* **92**, 234 (2007).

19. C. Hara, M. Matsuo, *Polymer*, **36**, 603 (1995).

20. M. Komatsu, T. Inoue, K. Miyasaka, *J. Polym. Sci. Phys. Ed.*, **24**, 303 (1986).

21. M. Liu, R. Cheng, R. Qian, *J. Polym. Sci. Part B : Polym. Phys.*, **33**, 1731 (1995).

22. P. Hong, C. Chou, C. He, *Polymer,* **42**, 6105 (2001).

23. J. C. J. F. Tacx, H. M. Schoffeleers, A. G. M. Brands, L. Teuwen, *Polymer,* **41**, 947 (2000).

24. R. P. A. Hartman, D. J. Brunner, D. M. A. Camelot, J. C. M. Marijnissen, and B. Scarlett, *J. Aero. Sci.,* **31**, 65 (2000).

25. C. A. Finch, *Poly(vinyl alcohol) Development*, Wiley, Chichester, UK, 1992.

26. L. Yao, T. W. Haas, A. Guiseppi-Elie, G. L. Bowlin, D. G. Simpson, G. E. Wnek, *Chem. Mater.*, **15**, 1860 (2003).

27. J. Zeleny, *Physical Review*, **3**, 69 (1914).

28. W. J. Morton, *US Patent 705691*, (1902).

29. P. K. Baumgarten, *J. Collo. Inter. Sci.*, **36**, 71 (1971).

30. L. Larrondo, R. St. John Manley, *J. Polym. Sci. : Polym. Phys.*, **19**, 909 (1981).

31. J. Doshi, D. H. Reneker, *J. Electrost.,* **35**, 151 (1995).

32. V. S. Praptowidodo, *J. Mol. Struct.,* **739**, 207 (2005).

33. L. B. Carvalho, A. M. Araujo, A. M. P. Almeida, W. M. Azevedo, *Sens. Actuators B Chem.,* **35**, 427 (1996).

34. S. Kurihara, S. Sakamaki, S. Mogi, T. Ogata, T. Nonaka, *Polymer,* **37**, 1123 (1996).

35. L. Gao, C. J. Seliskar, *Chem. Mater.,* **10**, 2481 (1998).

36. K. K. H. Wong, M. Z. Allmang, W. K. Wan, *J. Mater. Sci.,* **45**, 2456 (2010).