Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 46 (2005) 9538–9543

polymer

www.elsevier.com/locate/polymer

Polymer Communication

Electrospinning and structural characterization of ultrafine poly(butylene succinate) fibers

Eun Hwan Jeong[a], Seung Soon Im[b], Ji Ho Youk[a,*]

[a]*Division of Nano-Systems, Department of Advanced Fiber Engineering, Inha University, Incheon 402-751, South Korea*
[b]*Department of Fiber and Polymer Engineering, Hanyang University, Seoul 133-791, South Korea*

Received 19 April 2005; received in revised form 6 July 2005; accepted 31 July 2005
Available online 19 August 2005

Abstract

Biodegradable ultrafine poly(butylene succinate) (PBS) fibers were continuously electrospun for the first time from PBS solutions in chloroform (CF)/2-chloroethanol (CE) (7/3, w/w), CF/CE (6/4, w/w), dichloromethane (DM)/CE (7/3, w/w), DM/CE (6/4, w/w), and CF/3-chloro-1-propanol (9/1, w/w). These mixed solvents had an appropriate evaporation rate for the continuous electrospinning of PBS. The ultrafine PBS fibers had very high crystallinity and their average diameters were in the range of 125–315 nm. The annealed ultrafine PBS fibers exhibited a lamellar stack morphology containing crystalline and amorphous layers.

Keywords: Poly(butylene succinate); Electrospinning; Crystallinity

1. Introduction

The demand for biodegradable polymers is continuously increasing due to the problem of global waste. One of the most promising biodegradable aliphatic polyesters, poly (butylene succinate) (PBS), whose the trade name is 'BIONOLLE', is produced by the polycondensation of 1, 4-butandiol with succinic acid. It can be fabricated into various products such as fibers, non-woven mats, and injection-molded products because it has excellent melt processability and thermal and chemical resistance [1–3]. Recently, PBS/layered silicate nanocomposites have been developed in order to enhance the properties of PBS and consequently extend its application fields [4–6]. These composites exhibited improved tensile and gas-barrier properties without any loss of biodegradability.

On the other hand, the electrospinning of ultrafine polymer fibers has attracted a great deal of attention. They can be used for separation filters for submicron particles, protective fabrics, wipes, wound dressing materials, tissue scaffolds, sensors, etc. [7–12]. The electrospinning of biodegradable and biocompatible poly(lactide) (PLA) and poly(lactide-*co*-glycolide) (PLGA) has been conducted after dissolving them in various solvents such as *N*,*N*-dimethyl formamide (DMF), DMF/dichloromethane (DM), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), chloroform (CF), CF/acetone for medical applications [11,13–16]. However, the electrospinning of biodegradable PBS has not yet been reported. It is known that PBS is soluble in CF, DM, HFIP, *o*-chlorobenzene, etc. [17,18]. Unfortunately, they either have very low boiling temperatures for continuous electrospinning or are unsuitable for commercial electrospinning. In the case of the electrospinning of cellulose acetate (CA), only short fibers with a 'beads on the string' morphology were obtained due to the low boiling temperature of acetone, which was used as a solvent of CA [19,20]. Therefore, for the electrospinning of PBS, it is necessary to find solvents with an appropriate evaporation rate. In this study, new solvent systems for the continuous electrospinning of PBS are reported for the first time along with the thermal and structural properties of ultrafine PBS fibers.

---

* Corresponding author. Tel.: +82 32 860 7498; fax: +82 32 873 0181.
E-mail address: youk@inha.ac.kr (J.H. Youk).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.07.100

2. Experimental part

2.1. Materials

PBS (EnPol, $M_n \approx 75{,}000$) was purchased from IRe chemicals Ltd. (Korea). CF, DM, 2-chloroethanol (CE), 3-chloro-1-propanol (3-CP), and 1-chloro-2-propanol (1-CP) were purchased from Aldrich and used without further purification.

2.2. Electrospinning of PBS

The electrospinning setup used in this study consisted of a syringe and needle (ID = 1.0 mm), an aluminum collecting plate, and a high voltage supply (Chungpa EMT, CPS-40K03). PBS solutions were electrospun at a positive voltage of 14 kV and a working distance of 18 cm (the distance between the needle tip and the collecting plate). All electrospinning procedures were carried out at 25 °C.

2.3. Hydrolytic degradation

The hydrolytic degradation of the ultrafine PBS fibers was carried out in a 1 N NaOH solution at 25 °C. An ultrafine PBS fiber mat with dimensions of $1 \times 40 \times 40\ \mathrm{mm}^3$ was put in a 1 N NaOH solution. After a predetermined time, the hydrolytically degraded PBS fiber mat was taken out, washed with distilled water and completely dried in a vacuum oven at 25 °C. The degree of degradation was determined form the weight loss:

$$\text{Weight loss } (\%) = \frac{W_0 - W_t}{W_0} \times 100 \qquad (1)$$

where W_0 is the dry weight before degradation and W_t is the dry weight at time t.

2.4. Measurements

The morphology of the electrospun fibers was observed by a scanning electron microscope (SEM, Hitachi S-4200) after gold coating. The average diameter was determined by analyzing the SEM images with a custom code image analysis program. The thermal properties of the PBS samples were characterized by conducting differential scanning calorimetry (DSC) measurements (Perkin–Elmer Pyris 1) at a heating rate of 10 °C/min under a nitrogen atmosphere. A wide angle X-ray scattering (WAXS) analysis was carried out using a Philips X'pert MPD X-ray diffractometer at a scan speed of 0.025°/s. The wavelength of the X-ray beam was 0.154 nm (Cu Kα radiation).

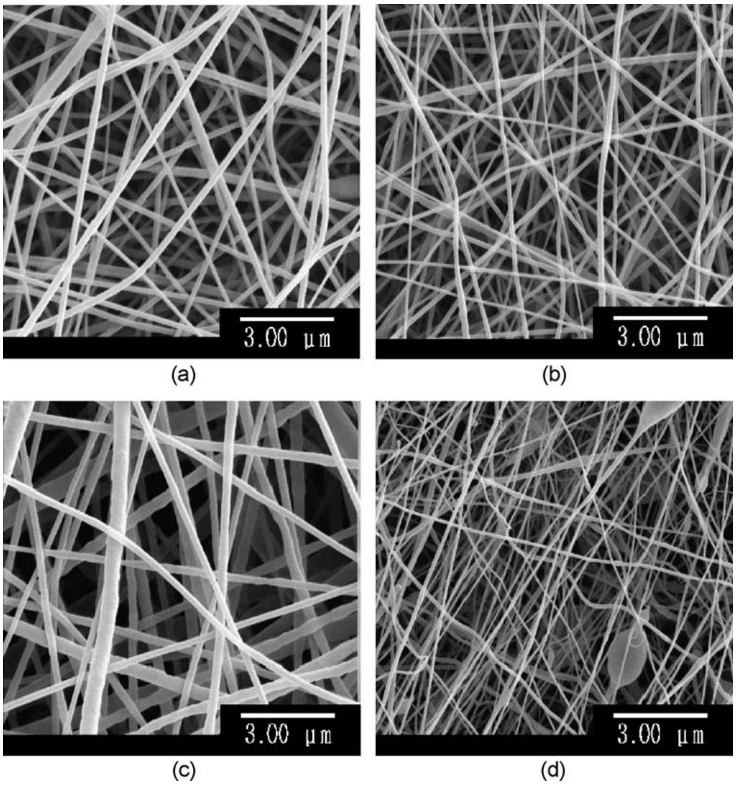
3. Results and discussion

In our previous study [21], ultrafine CA fibers were successfully prepared via the electrospinning of CA in a mixed solvent consisting of acetone and water. Only beaded short fibers could be obtained from the electrospinning of CA in acetone alone due to its fast evaporation. Although water is not a solvent for CA, using a mixture of acetone and water, ultrafine CA fibers were continuously electrospun at water contents of up to 15 wt%. Similarly, the electrospinning of PBS dissolved in CF and DM was unsuccessful because the gelation of the PBS solutions caused by their fast evaporation blocked the electrospinning needle. In order to decrease the evaporation rate of the solvent, various mixed solvent systems were tested and fortunately, suitable mixed solvent systems were found. As listed in Table 1, long uniform ultrafine PBS fibers were able to be continuously electrospun from PBS solutions in CF/CE(7/3), CF/CE(6/4), DM/CE(7/3), DM/CE(6/4), and CF/3-CP(9/1). The polymer concentration and solution flow rate were varied and optimized, in order to obtain the finest PBS fibers at a given positive voltage (14 kV) and working distance (18 cm). Fig. 1 shows representative SEM images of the ultrafine PBS fibers electrospun from various mixed solvents. The morphologies of the ultrafine PBS fibers obtained were very similar to each other for all of the mixed solvents. The average diameters of the PBS fibers were ranged from 125 to 315 nm. In the solvent systems consisting of DM/CE(5/5), CF/1-CP(9/1), DM/3-CP(9/1), and DM/1-CP(9/1), some of the PBS fibers had a 'beads on the string' morphology (Fig. 1(d)), probably due to the poor solubility of PBS in these solvents. PBS is not soluble in CE, 1-CP, or 3-CP and these solvents have boiling temperatures of 130, 126, and 161 °C, respectively. Although the presence of these solvents in the mixed solvents with CF and DM decreased the solubility of PBS, they nevertheless had an appropriate evaporation rate for the electrospinning of PBS.

The thermal properties of the as-prepared and annealed ultrafine PBS fibers were characterized using DSC and

Table 1
Electrospinning conditions for ultrafine PBS fibers in various mixed solvents

Solvent (w/w)	Polymer conc. (wt%)	Flow rate (mL/h)	Average fiber diameter (nm)	Product
CF/CE (7/3)	13	0.7	255	Fibers
CF/CE (6/4)	13	0.7	200	Fibers
DM/CE (7/3)	15	1.0	315	Fibers
DM/CE (6/4)	15	0.5	125	Fibers
DM/CE (5/5)	15	0.3	50	Beaded fibers
CF/3-CP (9/1)	15	1.5	315	Fibers
CF/1-CP (9/1)	15	1.0	100	Beaded fibers
DM/3-CP (9/1)	15	1.0	95	Beaded fibers
DM/1-CP (9/1)	15	0.6	90	Beaded fibers



(a) (b) (c) (d)

Fig. 1. SEM images of the ultrafine PBS fibers electrospun from various solvents: (a) CF/CE (6/4), (b) DM/CE (6/4), (c) CF/3-CP (9/1), and (d) DM/1-CP (9/1).

WAXD (Figs. 2 and 3). These PBS fibers were prepared by the electrospinning of 13 wt% PBS solution in CF/CE(7/3) and annealed under vacuum at 95 °C for 4 days. The as-prepared and annealed PBS fibers melted at around 113 °C and had a monoclinic unit cell structure with the characteristic WAXD peaks at 19.6 and 22.6°, which were assigned to the (020) and (110) planes, respectively [22]. As summarized in Table 2, the thermal properties of the ultrafine PBS fibers were very similar to each other, irrespective of the mixed solvent used for electrospinning. The ultrafine PBS fibers showed very high crystallinity, as compared to those of ultrafine fibers of common polymers [13,14,23–25]. It was reported that the crystallization of electrospun polymer was retarded because the rapid solidification of polymer chains hindered the formation of crystals. However, although the crystallization of the

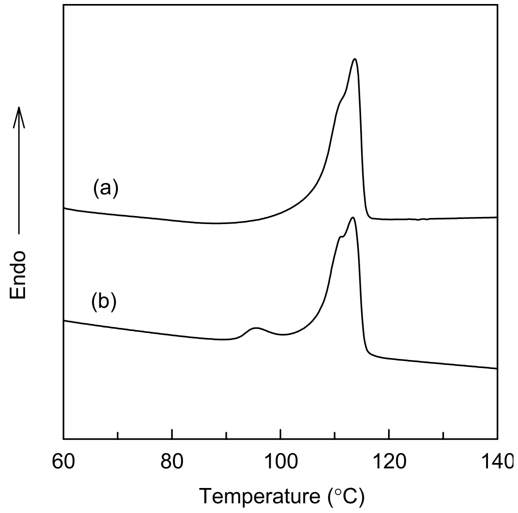


Fig. 2. DSC thermograms of (a) as-prepared and (b) annealed ultrafine PBS fibers.

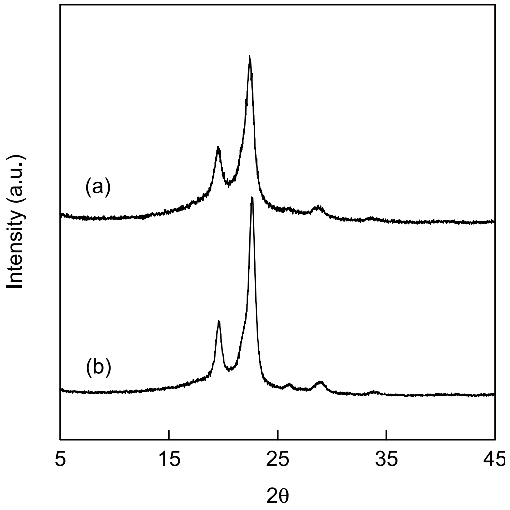


Fig. 3. WAXS patterns of (a) as-prepared and (b) annealed ultrafine PBS fibers.

Table 2
Thermal properties of ultrafine PBS fibers

Solvent (w/w)	T_m (°C)	ΔH_m (J/g)	Crystallinity (%)
CF/CE (7/3)	113.7	75.7	37.9
CF/CE (7/3)[a]	113.4	83.8	41.9
CF/CE (6/4)	113.5	74.7	37.4
DM/CE (7/3)	113.6	76.5	38.3
DM/CE (6/4)	113.5	74.0	37.0
CF/3-CP (9/1)	114.0	76.2	38.1

[a] Annealed at 95 °C for 4 days.

electrospun PBS was retarded, the ultrafine PBS fibers showed 37.9% crystallinity due to its own high crystallization rate [17,26,27]. The crystallinity of the PBS was calculated on the basis of the heat of fusion for PBS being 200 J/g [26]. Cho et al. [27] reported that the crystallinity of ice-quenched PBS film was as high as 31.7% (a value which was recalculated in this study). After the annealing of the ultrafine PBS fibers at 95 °C for 4 days, their crystallinity was increased to 41.9%.

The degradation of aliphatic polyesters takes place through the hydrolysis of the ester backbone under aqueous conditions, and their degradation rate depends on the crystallinity, the size and form of the crystallite, the morphological structure, etc. [28]. This hydrolytic degradation occurs preferentially in the amorphous region rather than the crystalline one, because water molecules can easily diffuse into the amorphous region of the polymer. The internal structure of the spherulites could be clearly observed from the enzymatic biodegradation of poly(β-hydroxybutyrate) and the hydrolytic degradation of PBS, after the preferential degradation in the amorphous regions [27,29]. In this study, the microstructure of the electrospun PBS fibers was investigated through the preferential degradation of the amorphous regions of the ultrafine PBS fibers. Fig. 4 shows the hydrolytic degradation of the as-prepared and annealed ultrafine PBS fibers in a 1 N NaOH solution. When PBS film (M_n=45,000) exhibiting 39.2% crystallinity (a value which was recalculated in this study) after annealing at 75 °C for 3 days was hydrolytically degraded in a 1 N NaOH solution at 25 °C, its weight loss was just 3% after 9 days [27]. On the other hand, the ultrafine PBS fibers were degraded very quickly under the same degradation conditions. This fast degradation of the ultrafine PBS fibers was attributed to their higher surface area. By taking into consideration the fast

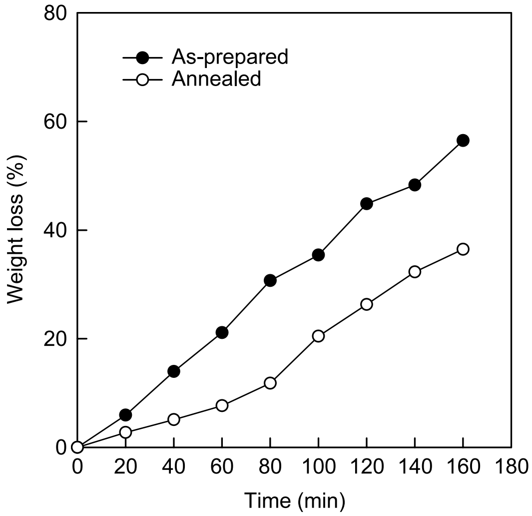


Fig. 4. Hydrolytic degradation of ultrafine PBS fibers in a 1 N NaOH solution.

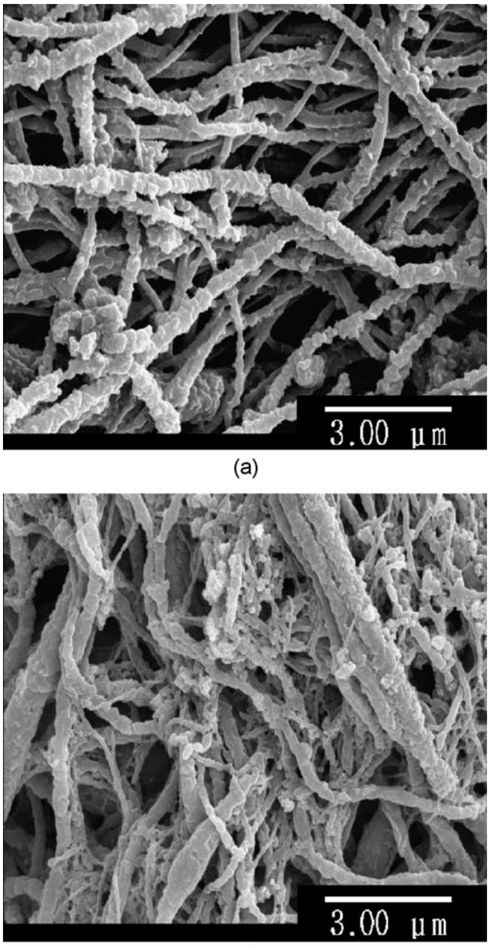


Fig. 5. SEM images of the as-prepared ultrafine PBS fibers after hydrolytic degradation in a 1 N NaOH solution for (a) 120 min and (b) 160 min.

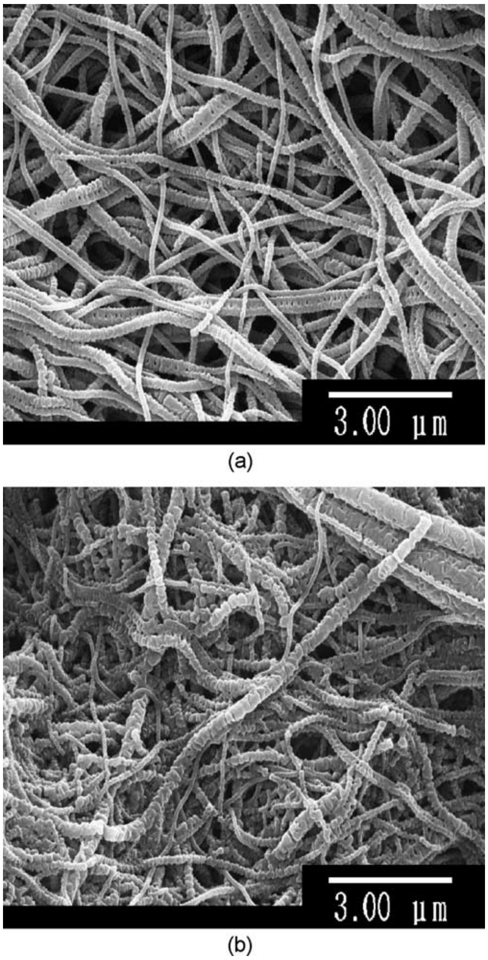


Fig. 6. SEM images of the annealed ultrafine PBS fibers after hydrolytic degradation in a 1 N NaOH solution for (a) 120 min and (b) 160 min.

biodegradability of ultrafine PBS fibers, it is expected that biodegradable ultrafine PBS fibers will be very useful for disposable separation filters for submicron particles, protective fabrics, and wipes, and that can replace the non-biodegradable fibers currently used for these applications.

The degradation rate of the annealed ultrafine PBS fibers was lower than that of the as-prepared ultrafine PBS fibers, indicating that the crystallinity of the ultrafine PBS fibers played an important role in their hydrolytic degradation. Figs. 5 and 6 show the SEM images of the as-prepared and annealed ultrafine PBS fibers after hydrolytic degradation, respectively. As the degradation proceeded, the surface of the fibers became coarse and the fibers ultimately broke down and finally turned into chunks. Also, some amorphous regions became aggregated, especially in the case of the as-prepared ultrafine PBS fibers. Interestingly, the hydrolytic degradation of the ultrafine PBS fibers occurred unevenly, as can be clearly observed in Fig. 6. The amorphous regions in the ultrafine PBS fibers were degraded first, while the crystalline ones remained. It seems that the crystalline layers were stacked between amorphous ones. Zong et al. [25] observed the structure and morphology changes of an electrospun PLGA nanofiber membrane during its in vitro degradation. The electrospun PLGA nanofibers were originally completely non-crystalline and rapidly crystallized, attaining a crystallinity of up to 50%, during the process of in vitro degradation. The authors suggested that a lamellar stack morphology containing crystalline and amorphous layers were developed and that the amorphous gaps existing between the lamellae stacks degraded first. A similar lamellar stack morphology was observed in the case of the ultrafine PBS fibers fabricated in this study, as shown in Fig. 6. Therefore, it is considered that the electrospun PBS fibers had lamellae, which were aligned with the fiber axis and lamellar stacks which were further developed after annealing.

Acknowledgements

This work was supported by Korea Research Foundation Grant (KRF-2004-003-D00490).

References

[1] Fujimaki T. Polym Degrad Stab 1998;59:209.
[2] Ratto JA, Stenhouse PJ, Auerbach M, Mitchell J, Farrell R. Polymer 1999;40:6777.
[3] Uesaka T, Nakane K, Maeda S, Ogihara T, Ogata N. Polymer 2000; 41:8449.
[4] Sinha Ray S, Okamoto K, Maiti P, Okamoto M. J Nanosci Nanotech 2002;2:171.
[5] Okamoto K, Sinha Ray S, Okamoto M. J Polym Sci, Polym Phys 2003;41:3160.
[6] Sinha Ray S, Okamoto K, Okamoto M. Macromolecules 2003;36: 2355.
[7] Spivak AF, Dzenis YA, Reneker DH. Mech Res Commun 2000;27: 37.
[8] Theron A, Zussman E, Yarin AL. Nanotechnology 2001;12:384.
[9] Huang L, Nagapundi K, Chaikof EL. J Biomater Sci, Polym Ed 2001; 12:979.
[10] Wang X, Drew C, Lee SH, Senecal KJ, Kumar J, Samuelson LA. Nano Lett 2002;2:1273.
[11] Li WJ, Laurencin CT, Caterson EJ, Tuan RS, Ko FK. J Biomed Mater Res 2002;60:613.
[12] Matthews JA, Wnek GE, Simpson DG, Bowlin GL. Biomacromolecules 2002;3:232.
[13] Zong X, Kim K, Fang D, Ran S, Hsiao BS, Chu B. Polymer 2002;43: 4403.
[14] Zong X, Ran S, Fang D, Hsiao BS, Chu B. Polymer 2003;44:4959.
[15] Kim K, Yu M, Zong X, Chiu J, Fang D, Seo YS, et al. Biomaterials 2003;24:4977.
[16] Zeng J, Chen X, Xu X, Liang Q, Bian X, Yang L, et al. J Appl Polym Sci 2003;89:1085.
[17] Yoo ES, Im SS. J Polym Sci, Polym Phys 1999;37:1357.
[18] Gan Z, Abe H, Kurokawa H, Doi Y. Biomacromolecules 2001;2:605.
[19] Liu H, Hsieh YL. J Polym Sci, Polym Phys Ed 2002;40:2119.
[20] Jaeger R, Bergshoef MM, Scholenherr H, Vancso GJ. Macromol Symp 1998;127:141.

[21] Son WK, Youk JH, Lee TS, Park WH. J Polym Sci, Polym Phys 2004;42:5.

[22] Ihn KJ, Yoo ES, Im SS. Macromolecules 1995;28:2460.

[23] Lee KH, Kim HY, Khil MS, Ra YM, Lee DR. Polymer 2003;44:1287.

[24] Zeng J, Chen X, Liang Q, Xu X, Jing X. Macromol Biosci 2004;4:1118.

[25] Zong X, Ran S, Kim K, Fang D, Hsiao BS, Chu B. Biomacromolecules 2003;4:416.

[26] Miyata T, Masuko T. Polymer 1998;39:1399.

[27] Cho K, Lee J, Kwon K. J Appl Polym Sci 2001;79:1025.

[28] You Y, Min BM, Lee SJ, Lee TS, Park WH. J Appl Polym Sci 2005;95:193.

[29] Tomasi G, Scandola M. Macromolecules 1996;29:507.