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Superstructure and mechanical properties of poly(L-lactic acid) microfibers prepared by CO_2 laser-thinning

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Abstract

Poly(L-lactic acid) (PLLA) microfibers were obtained by a carbon dioxide (CO_2) laser-thinning method. A laser-thinning apparatus used to continuously prepare microfibers was developed in our laboratory; it consisted of spools supplying and winding the fibers, a continuous-wave CO_2-laser emitter, a system supplying the fibers, and a traverse. The laser-thinning apparatus produced PLLA microfibers in the range of 100–800 m min^{-1}. The diameter of the microfibers decreased as the winding speed increased, and the birefringence increased as the winding speed increased. When microfibers, obtained through the laser irradiation (at a laser power of 8.0 W cm^{-2}) of the original fiber supplied at 0.4 m min^{-1}, were wound at 800 m min^{-1}, they had a diameter of 1.37 μm and a birefringence of 24.1×10^{-3}. The draw ratio calculated from the supplying and winding speeds was 2000×. The degree of crystal orientation increased with increasing the winding speed. Scanning electron microscopy showed that the microfibers obtained with the laser-thinning apparatus had smooth surfaces not roughened by laser ablation that were uniform in diameter. The PLLA microfiber, which was obtained under an optimum condition, had a Young's modulus of 5.8 GPa and tensile strength of 0.75 GPa.

Keywords: Poly(L-lactic acid); Microfiber; SEM

1. Introduction

Poly(L-lactic acid) (PLLA) that is one of the most biodegradable polymers, is a melt-spinnable polymer. The PLLA is of great interesting from the viewpoint of environmental protection and temporary medical application. The PLLA fiber has been studied by several investigators [1–5]. In many studies the primary aim is to improve its mechanical properties by a high speed melt spinning, drawing, and annealing [6–9]. The high-strength PLLA fiber with a Young's modulus of 16 GPa and tensile strength of 2.1 GPa was produced by dry spinning of a PLLA solution and a hot-drawing [8]. Melt spinning and drawing method prepared the PLLA fiber having a Young's modulus of 9 GPa and tensile strength of 0.87 GPa [9].

On the other hand, microfibers are very valuable from the viewpoint of industrial and medical materials and are now manufactured with highly skilled techniques, such as conjugate spinning (requiring a highly complex spinneret), islands-in-a-sea fiber spinning, melt blowing, and flash spinning. Poly(ethylene terephthalate) (PET), nylon 6, and isotactic polypropylene (i-PP) microfibers are produced by these methods and used as a wiping cloth, a filter, etc.

Laser-thinning method developed by us could easily produce microfibers by irradiating a continuous-wave carbon dioxide (CO_2) laser to fibers, such as PET, [10–12] nylon 6, [13] and i-PP [14] fibers, without highly skilled techniques. The developed apparatus using for the laser-thinning method could wind microfibers as monofilaments in the winding speed range of 100–2500 m min^{-1}. It is possible to thin not only all thermoplastic polymers but also an aramid fiber with the developed apparatus without a large-scale instrument used in the conventional processing.

The laser-thinning method was applied to as-spun PLLA fibers to produce PLLA microfibers, and could produce the PLLA microfibers in the same manner as PET, nylon 6, and it-PP fibers. The PLLA microfibers will become a great interesting material from the viewpoint of industrial and medical materials.

In this study, the superstructure and mechanical

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properties of the PLLA microfibers obtained at various laser-thinning conditions will be discussed in detail.

2. Experimental

2.1. Material

The original fiber used in this study was an as-spun PLLA fiber with $M_n = 80{,}000$ and $M_w = 140{,}000$ supplied by UNITIKA LTD. (Osaka, Japan). The original fiber had a diameter of 75 μm and birefringence of 6.3×10^{-3}. The glass transition temperature (T_g) and melting point (T_m) of the as-received fiber, as measured by differential scanning calorimetry (d.s.c.), were 57 and 178 °C, respectively. The original fiber was found to be slightly oriented fiber from a wide-angle X-ray diffraction (WAXD) pattern as shown in Fig. 1.

2.2. Measurements

The birefringence was measured with a polarizing microscope equipped with a Berek compensator (Olympus Optical Co., Ltd., Tokyo, Japan).

Scanning electron microscopy (SEM) micrographs of the fibers were taken with a JSM6060LV (JEUL Ltd., Tokyo, Japan) with an acceleration voltage of 4 kV.

Infrared measurements were made on a Fourier transform infrared (FTIR) microscope (Spectratech, Ltd. IR ms/SIRM) at a resolution of 4 cm^{-1}. Each spectrum resulted from an accumulation of 1024 scans.

Wide angle X-ray diffraction (WAXD) images of the fibers were taken with an imaging-plat (IP) film and an IP detector R-AXIS DS3C (Rigaku Co., Akishima Japan). The IP film was attached to a X-ray generator (Rigaku Co., Akishima, Japan) operated at 40 kV and 35 mA. The radiation was Ni-filtered Cu K_α. The sample-to-IP film distance was 65 mm. The fibers were exposed for 30 min to the X-ray beam from a pinhole collimator with a diameter of 1.0 mm.

The d.s.c. measurements were carried out using a THERM PLUS 2 DSC 8230C calorimeter (Rigaku Co., Akishima, Japan). The d.s.c. scans were performed within the temperature range of 25 to 200 °C, using a heating rate of 10 °C min^{-1}. All d.s.c. experiments were carried out under a nitrogen purge. The d.s.c. instrument was calibrated with indium.

Tensile properties were measured at 23 °C and a relative humidity of 50% with EZ Graph (Shimadzu Co. Ltd, Kyoto Japan). A gauge length of 20 mm and elongation rate of 10 mm min^{-1} were used. The experimental results are the average of 10 measurements.

2.3. CO_2 laser-thinning apparatus

The laser-thinning apparatus used to continuously produce the microfiber consisted of spools supplying and winding the fiber, a continuous-wave CO_2-laser emitter (PIN10S, Onizca Glass, Ltd., Oume, Japan), a system supplying the fiber, and a traverse as shown in Fig. 2. The continuous-wave CO_2 laser emitted light at 10.6 μm, and the laser beam had a 4.0-mm diameter. The power density was measured with a power meter during the laser irradiation. It was necessary to supply the fiber to a laser-irradiation point at a constant speed to prepare the microfiber in a stable manner. The supplying system pulled the original fiber from the supplying spool and supplied it to the laser-irradiation point at a constant speed. The supplying system played an important role in the continuous-laser-thinning apparatus. The fiber thinned at the laser irradiating point was wound on the spool at a winding speed of 100–2500 m min^{-1}.

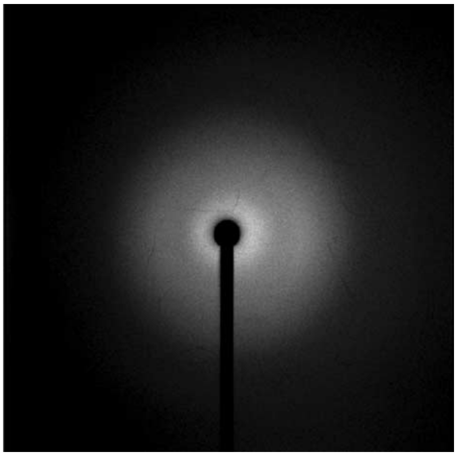


Fig. 1. Wide-angle X-ray diffraction pattern of PLLA original fiber.

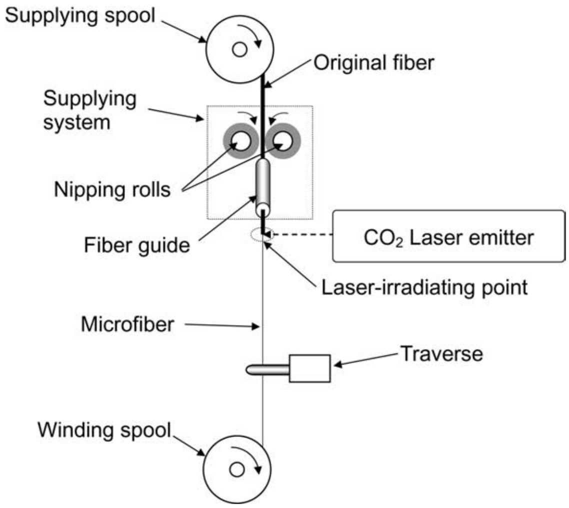


Fig. 2. CO_2 laser-thinning apparatus used for producing the microfiber.

3. Results and discussion

The diameter of microfiber was depended on the supplying speed of the original fiber, the laser power density, and the speed winding up the obtained microfiber. There is close relationship between the power density and supplying speed [14]. In the preparatory experiment, when the PLLA fiber obtained by irradiating the laser at a power density of 8.0 W cm^{-2} to the original fiber supplied at the speed less than 1 m min^{-1} was wound up at speed less than 1000 m min^{-1}, the microfiber with in the diameter range of 1–6 μm was found be produced.

Figs. 3 and 4 show the winding speed dependence of the diameter and birefringence of the microfibers obtained by three different supplying speeds. The maximum winding speed in the laser-thinning of the PLLA fiber is 800 m min^{-1}, and the laser-thinning at winding speed exceeding 800 m min^{-1} tends to be short of stability at producing the microfiber. The maximum winding speed of the PLLA fiber is smaller than that (maximum winding speed = 2000 m min^{-1}) for the PET fiber [12] and is almost equivalent to that (maximum winding speed = 848 m min^{-1}) for nylon 6 fiber [13]. In the winding speed dependence of the diameter at each supplying speed, the diameter decreased as the winding speed increased. The supplying speed dependence of the diameter became small with increasing the winding speed. When the microfiber, obtained through the laser irradiation of the original fiber supplied at 0.4 m min^{-1}, was wound on the spool at 800 m min^{-1}, the thinnest microfiber, with a diameter of 1.37 μm, was obtained. The draw ratio calculated from the supplying and winding speeds was 2000×. Such a high draw ratio was not previously attained by any drawing method.

In the winding speed dependence of the birefringence, the birefringence at each supplying speed increased with increasing the winding speed. The birefringence of the microfiber wound at 800 m min^{-1} was about 24.1×10^{-3} and is about 80% of the intrinsic crystallite birefringence (30×10^{-3}) of the PLLA[15]. The increase of birefringence shows the increase in the degree of amorphous and crystal orientation and in the degree of crystallinity because the total birefringence is the sum of an intrinsic crystallite birefringence and an intrinsic amorphous birefringence [16].

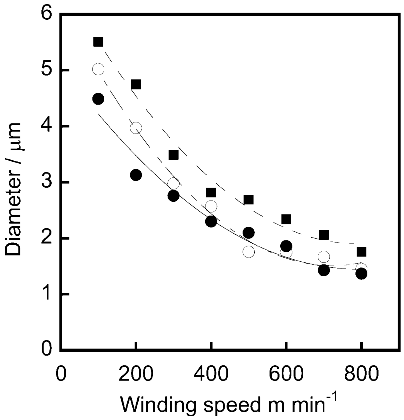


Fig. 3. Winding speed dependence of the diameter of the PLLA microfibers obtained at various supplying speeds: ● 0.4, ○ 0.5, ■ 0.6 m min^{-1}.

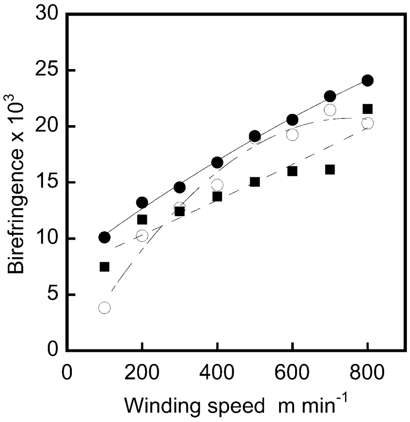
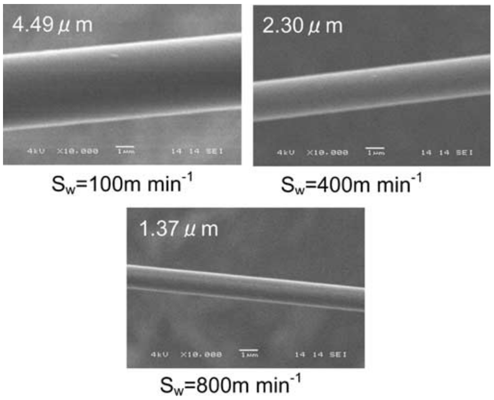


Fig. 4. Winding speed dependence of the birefringence of the PLLA microfibers obtained at various supplying speeds: ● 0.4, ○ 0.5, ■ 0.6 m min^{-1}.

Fig. 5 shows SEM photographs of microfibers wound at 100, 400, and 800 m min^{-1}. These microfibers were obtained through the laser irradiation of the original fiber supplied at 0.4 m min^{-1}. SEM at 10,000× showed that these microfibers had smooth surfaces not roughened by laser ablation that were uniform in diameter.

The PLLA crystallizes in two polymorphic forms: α form (orthorhombic) and β form (trigonal) [17–19]. The α form has 10/7 helix and is can be obtained by crystallization from the melt or from solution. The α-β crystal transition was taken place by hot drawing and solid-state extrusion [18–20]. Fig. 6 shows the bands at 923 cm^{-1} due to the α form [22,23] and at 912 cm^{-1} due to a β form (3/2 helix) observed in the original fiber and the microfibers obtained by various winding speeds. The bands at 923 and 912 cm^{-1} are assigned to the CH_3 rocking mode of the α and β forms,



S_w=100m min^{-1} S_w=400m min^{-1}

S_w=800m min^{-1}

Fig. 5. SEM photographs of 10,000 magnifications for the microfibers wound up at three different winding speeds (S_w).

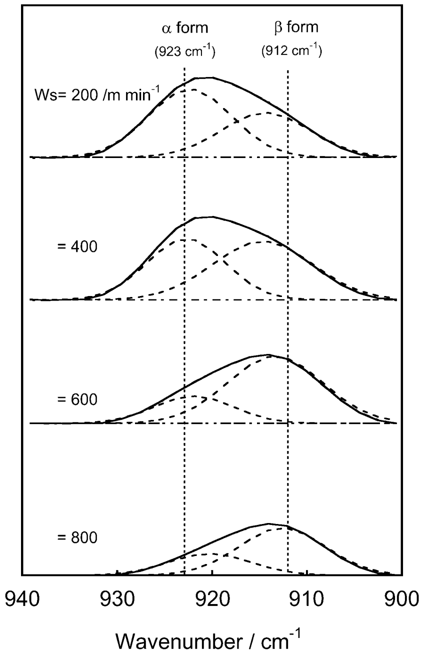


Fig. 6. FTIR spectra of the original fiber and the microfibers obtained by various winding speeds in a spectral range of 900–940 cm^{-1}(S_s= 0.4 m min^{-1}).

respectively [21,23]. The β form content increased with increasing the winding speed, and the α-β crystal transition was taken place at the higher winding speed.

Fig. 7 shows WAXD patterns of microfibers wound at a series of winding speeds. These microfibers were obtained through the laser irradiation of the original fiber supplied at 0.4 m min^{-1}. No reflection due to oriented crystallites is observed in the WAXD pattern of the microfiber wound at 100 m min^{-1}. The WAXD patterns of microfibers wound at 200, 600, and 800 m min^{-1} show strong equatorial reflections due to the highly oriented crystallites, and the strong equatorial reflections is attributable to the (0010)α reflection of α form crystal. The WAXD of the microfiber obtained at 800 m min^{-1} shows the {(0010)α+(023)β} doublet and the (003)β slight reflection of β form crystal on the lower 2θ side of the doublet reflection.

Fig. 8 shows the degree of crystallites orientation estimated from the half-width of the meridian the (0010)α reflection peak. In spite of the low winding speed, the highly oriented crystallites were formed by the flow-induced crystallization, and the degree of crystal orientation is tending to increase slightly with increasing winding speed. This fact indicates that not only the molecular flow but also the molecular orientation and crystallization are induced by the higher strain rate during the thinning process and that agrees approximately with the result of birefringence mentioned above.

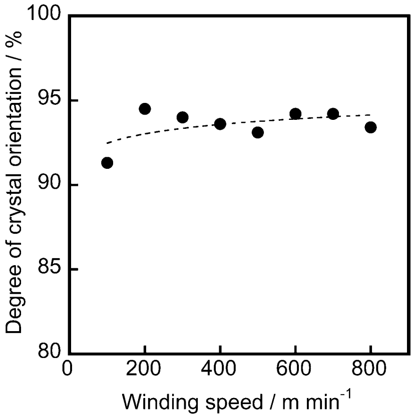
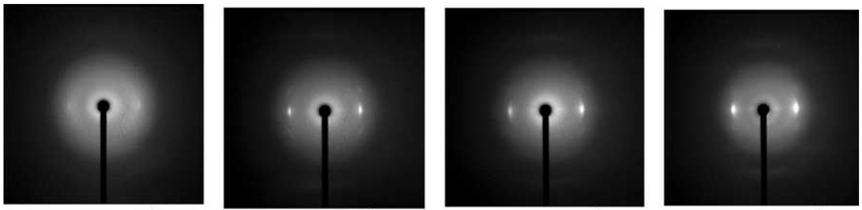


Fig. 8. Winding speed dependence of degree of crystallites orientation estimated from the half-width of the meridian the (0010)α reflection peak for the microfibers obtained at S_s=0.4 m min^{-1}.

Fig. 9 shows d.s.c. curves for the original fiber and the microfibers wound up at a series of winding speeds. The original PLLA fiber shows a change in slope in the specific heat at 62 °C, which corresponds to the glass transition; an exothermic transition at 90 °C caused by a cold crystallization; and a broad melting endotherm peaking at 166 °C. Its melting peak can be ascribed to the lamellar crystals of α form which crystallized during the d.s.c. scanning [24,25] because the α form was obtained by crystallization from the melt. No melting peak of the β form, which is about 10 °C lower than that of the α crystal [26], is observed in the d.s.c. curve of the original fiber.

The microfibers obtained at a series of winding speeds have the cold crystallization temperature (T_{cc}) of 72 °C, a melting endotherm peaking in the vicinity of 166–170 °C, and the trace of shoulder on the lower temperature side of their peaks, but the melting peak due to the β form was not observed in the d.s.c. curves of the microfibers. The T_{cc} of the microfibers is 18 °C lower than the T_{cc} of the original fiber. The decrease in the T_{cc} was caused by the increase in the degree of orientation of amorphous chains. The melting temperature (T_m) of the microfibers is 3–4 °C higher than



100m·min^{-1} 200m·min^{-1} 600 m·min^{-1} 800m·min^{-1}

Fig. 7. Wide-angle X-ray diffraction patterns of the PLLA microfibers wound up at 100, 200, 600, and 800 m min^{-1}.

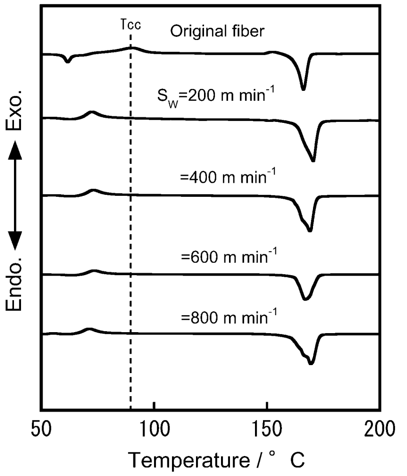


Fig. 9. D.s.c. curves of the original fiber and the microfibers wound up at various winding speeds ($S_s = 0.4$ m min^{-1}).

the T_m of the original fiber. The appearance of the shoulder on the lower temperature side of the melting peak is based on the fringed-micelle α crystals formed by the flow-induced crystallization. Elenga et al. [27] suggested from the standpoint of kinetics that the low-temperature melting peak was ascribed to the fringed-micelle crystals built up by chain unfolding, and the high-temperature one corresponds to the untransformed fraction of the lamellar crystals that undergo reorganization during the heating scan. The melting peaks can be attributed to melting of the lamellar crystal recrystallized from the α and β crystals with low levels of crystal perfection during the DSC measurement.

Figs. 10 and 11 show the changes in Young's modulus and tensile strength of the microfibers laser-irradiated by three different supplying speeds with the winding speed. In the winding speed dependence of Young's modulus and the tensile strength at each supplying speed, these values increased as the winding speed increased. The influence of the supplying speed on the mechanical properties became large as the winding speed increased. When the microfibers, obtained through the laser irradiation of the original fiber supplied at 0.4 m min^{-1}, were wound on the spool at 800 m min^{-1}, the microfiber with a Young's modulus of 5.8 GPa and a tensile strength of 0.75 GPa, was obtained.

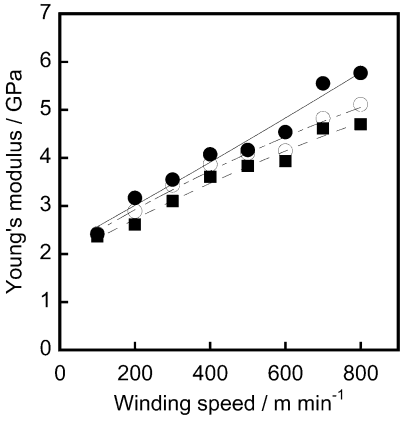


Fig. 10. Winding speed dependence of Young's modulus of the PLLA microfibers obtained at various supplying speeds: ● 0.4, ○ 0.5, ■ 0.6 m min^{-1}.

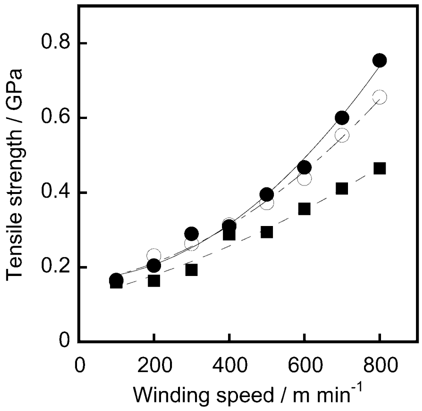


Fig. 11. Winding speed dependence of the tensile strength of the PLLA microfibers obtained at various supplying speeds: ● 0.4, ○ 0.5, ■ 0.6 m min^{-1}.

The CO_2 laser-thinning mechanism could be considered as follows. When the original fiber, supplied to the laser-irradiation point by the supplying system, was heated through the irradiation of a high-output-power laser, the plastic viscosity of the fiber irradiated by the laser became sufficiently low, and a portion of the fiber was nearly molten. The original fiber was continuously thinned by the plastic flow occurring from the nearly molten state, and then the microfiber, having fallen down because of its own weight, was wound on the winding spool. Rapidly winding the microfiber obtained through laser irradiation of the fiber supplied at the lower speed induced large deformation at a faster strain rate, and such deformation increased the degree of molecular orientation and caused a flow-induced crystallization.

4. Conclusions

The CO_2 laser-thinning method was applied to the PLLA fiber to continuously prepare the as-spun PLLA microfiber. The apparatus made it possible to continuously wind the microfiber on the spool at the high winding speed. In the winding speed dependence of the diameter and the birefringence, the diameter decreased with increasing winding speed, and the birefringence increased with increasing the winding speed. The thinner the microfiber, the higher was birefringence. When the microfiber obtained by irradiating the laser to the original fiber supplied at 0.40 m min^{-1} was wound at a winding speed of 800 m min^{-1}, the thinnest microfiber with a diameter of 1.37 μm was obtained, its birefringence was 24.1×10^{-3}, Young's modulus 5.8 GPa, and a tensile strength 0.75 GPa.

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References

[1] Jamshidi K, Hyon SH, Ikeda Y. Polymer 1988;29:2229.
[2] Perego G, Cella GD, Bastioli C. J Appl Polym Sci 1996;59:37.
[3] Iannace S, Maffezzoli A, Leo G, Nicolais L. Polymer 2001;42:3799.
[4] Blomqvist J, Mannfors B, Pietia L-O. Polymer 2002;43:4571.
[5] Suesat J, Phillips DAS, Wilding MA, Farrington DW. Polymer 2004;44:2229.
[6] Shmack G, Tandler B, Vogel R, Beyreuther R, Jacobsen S, Fritz H-G. J Appl Polym Sci 1999;73:2785.
[7] Cicero JA, Dorgan JR, Janzen J, Garrett J, Runt J, Lin JS. J Appl Polym Sci 2002;86:2828.
[8] Leenslag WJ, Gogolewski S, Pennings AJ. J Appl Polym Sci 1984;29:2829.
[9] Leenslag WJ, Pennings AJ. Polymer 1987;28:1695.
[10] Suzuki A, Mochizuki N. J Appl Polym Sci 2003;88:3279.
[11] Suzuki A, Mochizuki N. J Appl Polym Sci 2003;90:1955.
[12] Suzuki A, Okano T. J Appl Polym Sci 2004;92:2989.
[13] Suzuki A, Kamata K. J Appl Polym Sci 2004;92:1449.
[14] Suzuki A, Narisue S. J Appl Polym Sci 2004;92:1534.
[15] Kobayashi J, Asahi T, Ichiki M, Oikawa H, Suzuki T, Watanabe E, et al. J Appl Phys 1995;77:2957.
[16] Stein RS, Norris FH. J Polym Sci 1956;21:381.
[17] Eling B, Gogolewski S, Pennings AJ. Polymer 1982;23:1587.
[18] Hoogsteen W, Postema AR, Pennings AJ. Macromolecules 1990;23:634.
[19] Miyata T, Masuko T. Polymer 1997;38:4003.
[20] Takahashi K, Sawai D, Yokoyama T, Kanamoto T, Hyon SH. Polymer 2004;45:4969.
[21] Sawai D, Takahashi K, Sasashige S, Kanamoto T, Hyon SH. Macromolecules 2003;36:3601.
[22] Lee JK, Lee KH, Jin BS. Eur Polym J 2001;37:907.
[23] Kang S, Hsu SL, Stidham HD, Smith PB, Leugers MA, Yang X. Macromolecules 2001;34:4542.
[24] Pecorini TJ, Hertzberg RW. Polymer 1993;34:5053.
[25] Quintanilla L, Rodríguez-Cabello JC, Pastor JM. Polymer 1994;35:2321.
[26] Sawai D, Takahashi K, Imamura T, Nakamura K, Kanamoto T, Hyon SH. J Polym Sci, Polym Phys 2002;40:95.
[27] Elenga R, Seguela R, Rietsch F. Polymer 1991;32:1975.