Synthesis and Characterization of Biodegradable Poly(1,4-butanediol succinate)

DAE KYUNG SONG and YONG KIEL SUNG*

Department of Chemistry, Dongguk University, Seoul 100-715, Korea

SYNOPSIS

Biodegradable poly(1,4-butanediol succinate) was synthesized from 1,4-butanediol and succinic anhydride. The synthesized polymer was identified by ^{1}H-NMR spectrometer and FT-IR spectrophotometer. The weight average molecular weights were between 4,600 and 29,000, and molecular weight distributions were in the range of 1.7 and 1.9. The glass transition temperature of poly(1,4-butanediol succinate) was revealed at 73°C. The crystallization and cold crystallization of the polymers were investigated as a function of heating rate, cooling rate, reheating rate, and molecular weight. The biodegradation behavior of poly(1,4-butanediol succinate) in micro-organisms such as fungi, actinomycetes, and bacteria was studied by using modified ASTM method. Based upon visual observation, the crystalline structure of films composed of larger molecular weight polymers retained their crystallinity longer than similar structures in low molecular weight samples. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Biodegradable polyesters derived from α-hydroxy acids and lactones are being used in an increasingly large number of biomedical applications, such as absorbable bone plates and other surgical fixation devices, bioabsorbable surgical suture, and carrier systems for the controlled release of drugs.[1-6]

The great importance of a biodegradable material relates to the biocompatibility, toxicity, and immunogenicity.[1,7] Additional requirements for some applications are predictable rate of biodegradation and suitable mechanical properties, and susceptible microbial and environmental degradation upon disposal without any adverse environmental impact.[8-10] The scarcity of polymers that meet these rather demanding requirements has prompted a continuous search for new, improved biodegradable polymers.

Recently, Fukuzaki et al.[11-13] synthesized low molecular weight polyesters by direct polycondensation in the absence of catalysts to get more pure materials. Crosslinked polyester matrix was prepared using Krebs cycle acid, and poly(β-malic acid) derivertives that have hydrophilicity and hydrophobicity were synthesized and characterized.[14-17]

The Krebs cycle acids are good candidates for the development of new polyesters.[14-17] The tricarboxylic acid cycle, or Krebs cycle, is the process during which acetal moiety, in acetal CoA, is oxidized completely to carbon dioxide and water. It is expected that polyester prepared using Krebs cycle acid derivatives is biocompatible and biodegradable, and the degradation residue will be nontoxic.

In this study, poly(1,4-butanediol succinate) was synthesized from 1,4-butanediol and succinic anhydride, which was a Krebs cycle acid derivative. The synthesized polymers were identified by ^{1}H-NMR spectrometer and FT-IR spectrophotometer. The molecular weights and molecular weight distributions of synthetic polymers were measured by gel permeation chromatography. The effects of cooling rate, reheating rate, crystallization time and temperature, and molecular weight were investigated on the poly(1,4-butanediol succinate). Biodegradation of poly(1,4-butanediol succinate) was also studied by microorganisms, which can meet in the environment and have broad substrate specificity using the modified American Standards for Testing and Materials (ASTM) agar plate method.[18]

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 56, 1381-1395 (1995)
 CCC 0021-8995/95/111381-15

EXPERIMENTAL

Synthesis

Succinic anhydride and 1,4-butanediol were purchased from Aldrich Chemical Co. *p*-Toluenesulfonic acid, which was used as a catalyst, was obtained from Sigma Chemical Co. 1,4-Butanediol, *p*-toluenesulfonic acid, and succinic anhydride were dissolved in toluene and placed in a two-necked flask equipped with a magnetic stirring bar, thermometer, and dean-stark trap on top of which is a condenser fitted with a drying tube. The reaction mixture is placed in an oil bath and maintained at reflux with stirring for a predetermined time. The reaction mixture was cooled and filtered. The residue was washed with acetone and recrystallized with chloroform and diethyl ether. The product was dried in vacuum at room temperature for 1 week.

Characterization

^{1}H-NMR spectra were recorded with a Varian Gemini 300 spectrometers using $CDCl_3$ as a solvent. IR spectrum was recorded on a Nicolet 5-MX FT-IR spectrophotometer in the solid state using a KBr pellet. Weight average molecular weight, number average molecular weight, and molecular weight distribution of the polymers were measured using a Shimadzu LC-9A system. The columns were calibrated with polystyrene standards, having a narrow molecular weight distribution. The glass transition temperatures (T_g), crystallization temperatures (T_c), and melting temperatures (T_m) of the polymers were measured with the differential scanning calorimetry Perkin-Elmer DSC-4 system. Calibration of the temperature was performed using an indium standard. Amorphous samples of poly(1,4-butanediol succinate) were prepared by melt at 150°C using the hot plate, holding for 5 min, then quenched by immersing in liquid N_2. For the studies of thermal history effects, samples were heated from 30 to 150°C at various heating rates and cooled from 150 to 30°C at various cooling rates. For the observation of the spherulitic structure, the sample was melted on a hot plate at 150°C for 5 min and slowly cooled to room temperature. The grown spherulites were observed using a Leitz Laborlux 12 Pol S polarizing microscope equipped with a 35 mm camera.

Table I Preparation of Nutrient-Salts Broth

Reagents	Weight
Potassium dihydrogen orthophosphate (KH_2PO_4)	0.7
Magnesium sulfate ($MgSO_4$ $7H_2O$)	0.7
Ammonium nitrate (NH_4NO_3)	1.0
Sodium chloride (NaCl)	0.005
Ferrous sulfate ($FeSO_4$ $7H_2O$)	0.002
Zinc sulfate ($ZnSO_4$ $7H_2O$)	0.002
Manganous sulfate ($MnSO_4$ $7H_2O$)	0.001

Biodegradation

The microorganisms for biodegradation test were *Aspergillus niger* and *Penicilium funicularium* as fungi, *Actinoplane spp* as actinomycetes, and *Pseudomonas fluorescens* as bacteria. *Aspergillus niger* and *Penicilium funicularium* are routinely used in the ASTM procedure for the determination of biodegradation. The conidia harvested from 7 days' culture slant were washed with distilled water three times. The harvested conidia were suspended in nutrient salt broth by 10^9 conidia/mL. The cell suspension of *Pseudomonas fluorescens* was prepared with distilled water and cell density was adjusted to 10^{12} cell/mL in nutrient salt broth. Mycelial fragmented propagule suspension of *Actinoplane spp* was prepared by homogenization of mycelia and adjusted to 2 mg/mL in nutrient salt broth. Nutrient salt broth was prepared by dissolving in 1 L of water the designated amounts of the reagents in Table I. The test medium was sterilized by autoclaving at 121°C for 20 min. The pH of the medium was adjusted by the addition of 0.01 *N* NaOH solution so that after sterilization the pH was 6.2. Acid-washed cover glasses for the microscope (18 × 18 mm) were flooded with 75 μL of poly(1,4-butanediol succinate)-chloroform solution at a concentration of 0.16 g/mL. Solvent was evaporated on the hot plate and the polymer film was cooled slowly to room temperature. Less than 40 μm thick poly(1,4-butanediol succinate) film was deposited on the glass. The prepared film was sterilized at 140°C for 4 h in a dry oven and placed on the agar plate. The prepared suspension of each microorganism was inoculated on the polymer film surface and incubated at 28°C. The polymer film on the cover glass was removed from the incubator after a predetermined time and the shape was observed using microscopy (×200). In the degraded samples by *Aspergillus niger*, the molecular weight decrease of PBS (M_w: 29,000) was also measured with GPC.

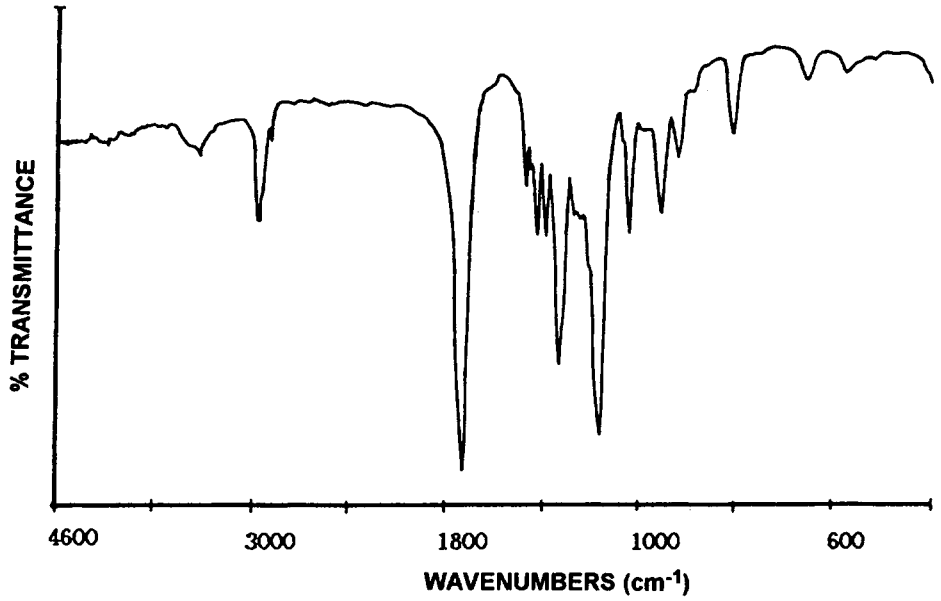

Figure 1 FT-IR spectrum of poly(1,4-butanediol succinate).

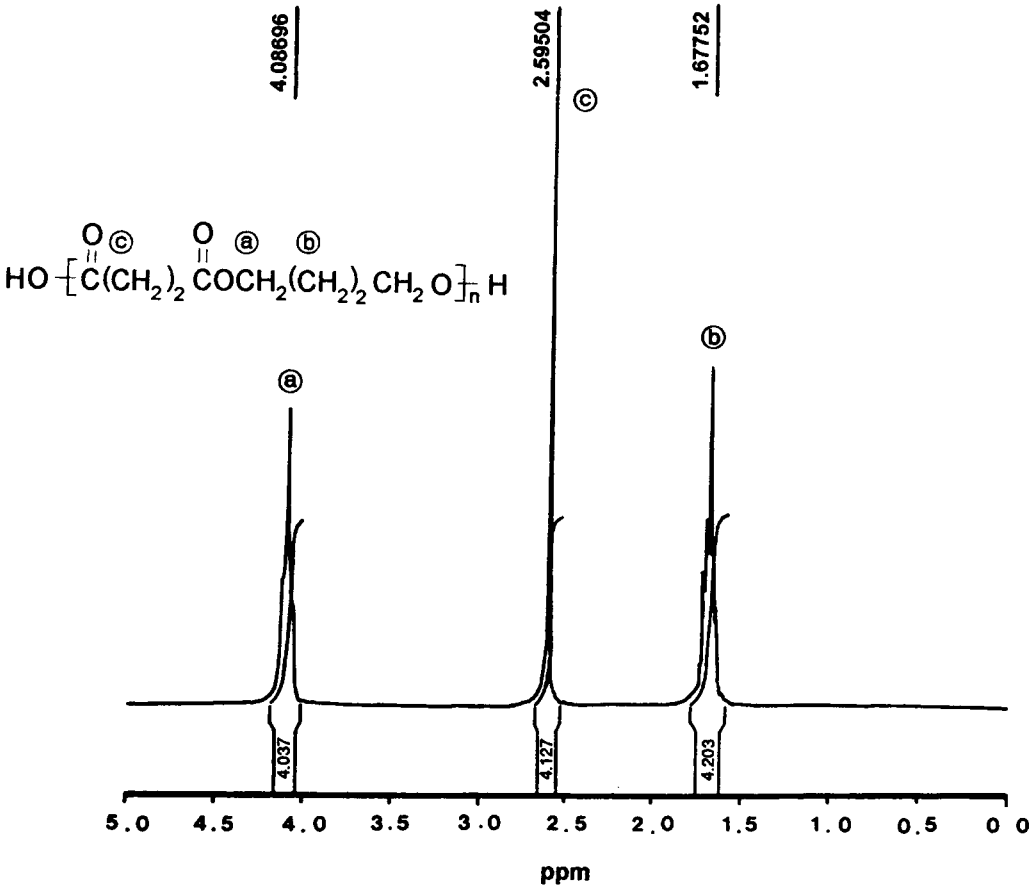

Figure 2 ^{1}H-NMR spectrum of poly(1,4-butanediol succinate).

RESULTS AND DISCUSSION

Identification

The FT-IR spectrum of the PBS is shown in Figure 1. IR vibrational band characteristic of ester bond formation is indicated by the presence of carbonyl peak at 1,740 cm^{-1}. In the NMR spectrum of PBS, three signals are shown at δ 4.1($-CH_2-$, peak[a] of 1,4-butanediol unit), δ 1.7($-CH_2-$, peak[b] of 1,4-butanediol unit), and δ 2.6($-CH_2-$, peak[c] of succinyl unit) (Fig. 2). The molar composition of PBS was estimated from the ratio of the areas of peak[a], peak[b], and peak[c], and the result agreed with the initial monomer composition, indicating that 1,4-butanediol reacted quantitatively with succinic anhydride in polycondensation.

M_n, M_w, and M_w/M_n were listed in Table II. The molecular weight distribution of each polymer, ranging from 1.7 to 1.9, was narrower than other polyesters, which were synthesized using hydrolysis of lactone or using oligomeric ester diol.[10-13,19]

Table II Molecular Weight and Molecular Weight Distribution of Poly(1,4-Butanediol Succinate)

	Synthetic Condition		GPC Results		
Sample	Reaction Time (h)	Mol % of Catalyst	M_n	M_w	MWD
PBS	3.33	0.4	2,700	4,600	1.69
	4.5	0.4	3,300	6,300	1.88
	12	0.4	5,700	11,000	1.92
	17	0.4	9,400	18,000	1.91
	20	0.4	16,000	29,000	1.82

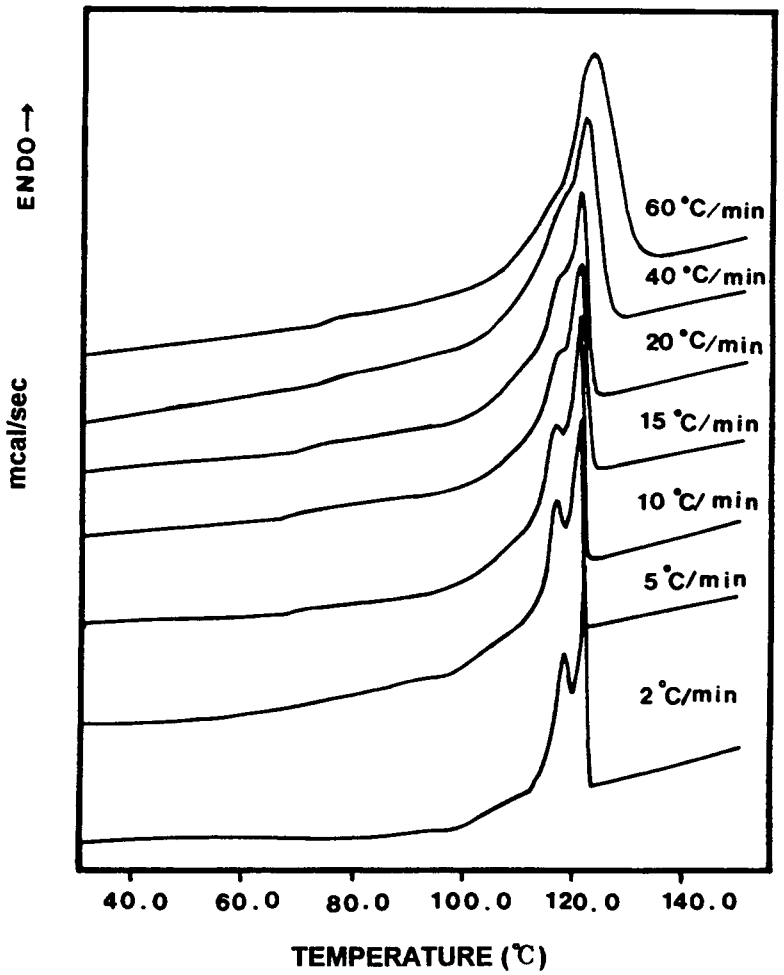

Figure 3 DSC melting curves of poly(1,4-butanediol succinate) (M_w: 18,000) as a function of heating rate.

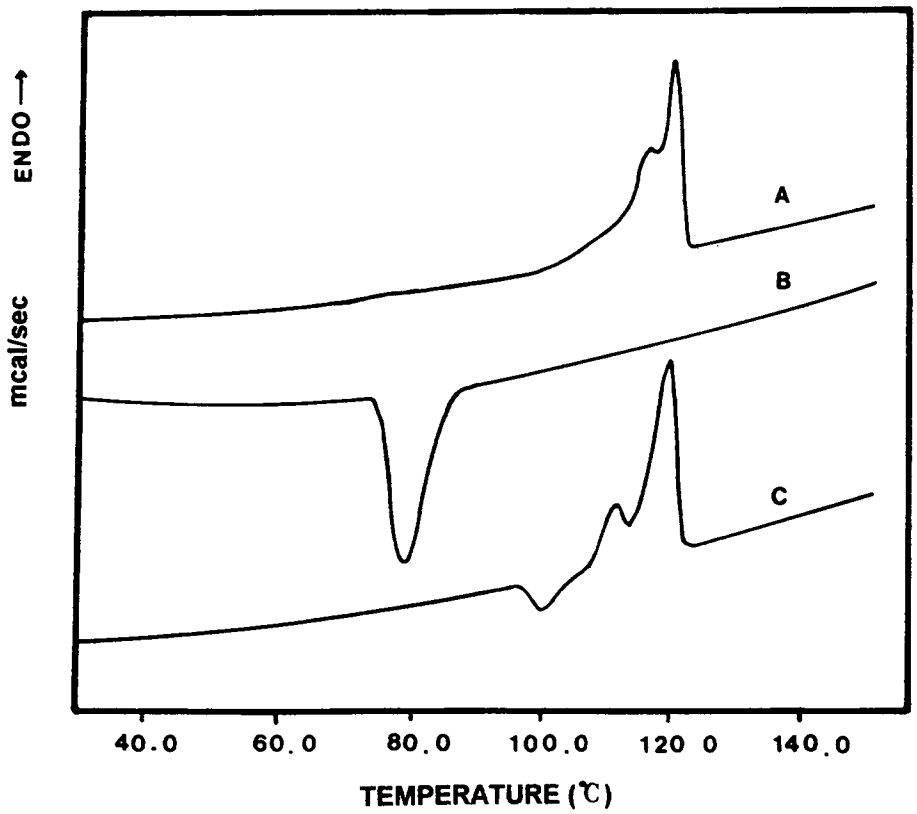

Figure 4 Typical DSC thermograms of poly(1,4-butanediol succinate) (M_w: 18,000): (A) First heating; (B) supercooling from the melt; (C) second heating of recrystallized polymer.

Characterization

The crystalline size and structure,[21-24] crystallization rate[25-29] and temperature,[30] degree of crystallinity[23-25] and nucleation density[31] were influenced by the thermal history in the melt state and the melt temperature, crystallization time and temperature, cooling rate, and the molecular weight of the polymer.

DSC thermograms of PBS are shown in Figure 3. When PBS was heated from 30°C to 150°C at various heating rates, 2, 5, 10, 15, 20, 40, and 60°C/min, T_g is shown at 73°C with multiple melting endotherms. So far, many investigations have been

Table III Quantitative Calculation for the Enthalpy Changes of Exothermic Parts in Supercooling Process and Cold Crystallization of the Second Heating Process and for the Enthalpy Change of Melting Endotherm in the Case of Different Molecular Weight

M_w \ ΔH	ΔHm (cal/g)	ΔHc (cal/g)	ΔHcc (cal/g)	ΔHc + ΔHcc (cal/g)
4,600	20.5	−18.1	−2.6	−20.7
6,300	22.3	−19.7	−2.7	−22.4
11,000	21.7	−19.4	−2.9	−22.3
18,000	21.8	−18.4	−3.2	−22.0
29,000	21.9	−18.7	−3.0	−21.7

ΔHm: enthalpy change of melting process.
ΔHc: enthalpy change of supercooling process.
ΔHcc: enthalpy change of cold crystallization in second heating.

Table IV The Enthalpy Changes and the Onset and Maximum Temperatures of the Crystallization Exotherm for Poly(1,4-Butanediol Succinate) on Cooling Process from the Melt in the DSC at Various Holding Times

Holding Time (h)	T_c, Onset (°C)	T_c, Max (°C)	ΔHc (cal/g)
0.08	83.3	78.3	−20.3
0.5	82.5	77.7	−20.4
1	81.8	77.0	−20.6
4	81.1	76.5	−19.9
8	80.1	75.4	−20.4
24	80.2	75.4	−20.2
48	80.8	75.5	−20.2
100	80.6	75.3	−20.1

Table V The Enthalpy Changes and Melting Temperatures of Poly(1,4-Butanediol Succinate)(M_w: 18,000) on Reating Process in DSC at Various Holding Time

Holding Time (h)	ΔHc (cal/g)	T_m (°C)
0.08	22.3	116.1
0.5	22.5	115.9
1	22.4	115.5
4	22.1	115.3
8	22.5	115.0
24	22.4	114.8
48	22.2	114.6
100	21.8	114.2

made to clarify the origin of the multiple melting endotherms.[32–37] The pair of melting peaks could arise from an initial single-peak crystal distribution that undergoes melting, recrystallization or reorganization, and remelt during the heating process. The lowest broad melting endotherm is due to the melting of crystals of poor quality that existed in the initial distribution. The middle endotherm is due to the maximum endotherm in the initial distribution. The highest temperature peak is due to the melting of the crystals formed by the recrystallization. Melting endotherms are not separated completely at higher scan rates.

Figure 4 shows DSC thermogram under step

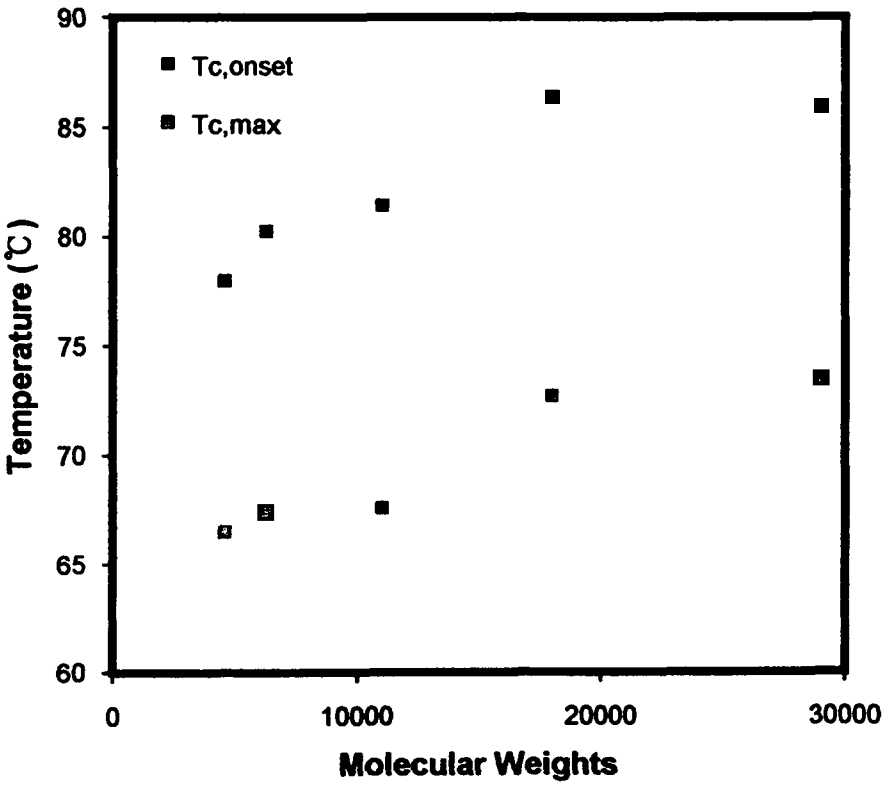

Figure 5 The onset temperature of crystallization and maximum crystallization temperature for various molecular weights of poly(1,4-butanediol succinate).

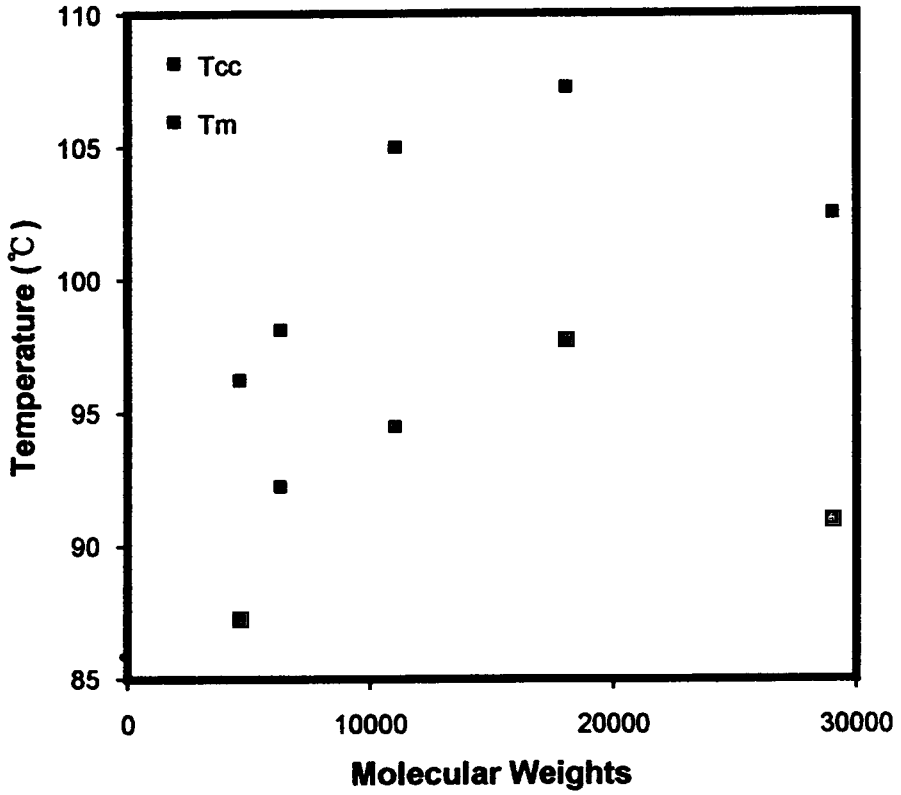

Figure 6 Cold crystallization temperatures and melting temperatures on reheating processes as a function of molecular weights.

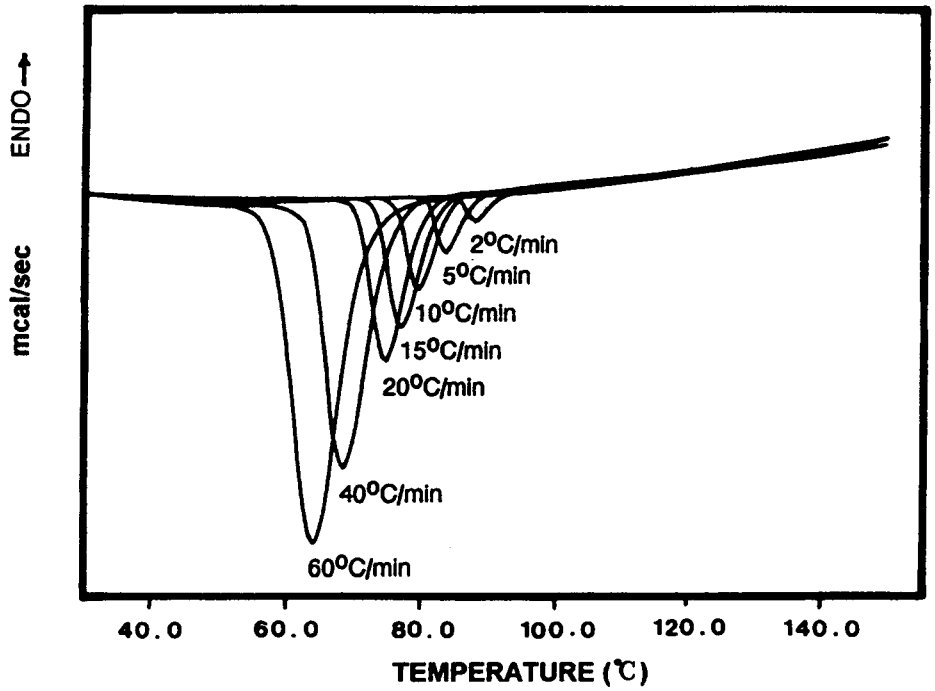

Figure 7 DSC cooling curves of poly(1,4-butanediol succinate) (M_w: 18,000) at various cooling rate.

heating process; sample was heated from 30 to 150°C at a heating rate of 10°C/min, holding for 5 min, and cooled to 30°C, and then reheated to 150°C at 20°C/min. In the reheating thermogram, cold crystallization exothermic peak and multimelting endothermic peaks are shown. The results of the analyses for enthalpy changes during crystallization, cold crystallization, and melting process are listed in Table III. The enthalpy changes for crystallization, cold crystallization, and melting process are 19 cal/g, 3 cal/g, and 22 cal/g, respectively. The sum of enthalpy changes for crystallization and cold crystallization are equal to the enthalpy change of the melting process. Enthalpy change for crystallization is about 86% of the sum of the enthalpy changes for crystallization and cold crystallization. It is considered that most of the crystals in polymer were formed during the cooling process.

For the study of the effect of holding time in melt state, poly(1,4-butanediol succinate) (M_w: 18,000) was melted at 150°C for various melt holding times then cooled to 30°C at 10°C/min and reheated to 150°C at 10°C/min. The onset temperatures of crystallization, maximum crystallization temperatures, and enthalpy changes for crystallization are listed in Table IV. The enthalpy changes and melting temperatures on reheating process are listed in Table V. Crystallization onset temperature and maximum crystalline temperature decreased to a small extent as holding time increased from 5 min to 8 h. No significant decrease in crystallization temperature occurred above 8 h and, thus, no significant enthalpy changes were observed. The melting temperature was not decreased significantly as the holding time increased. Enthalpy changes in the melting process did not occur at various holding times in the melt state. It is considered that previous crystalline nuclei were destroyed after 5 min holding at 150°C. Chain scission and/or crosslinking did not occur during the melt state holding.

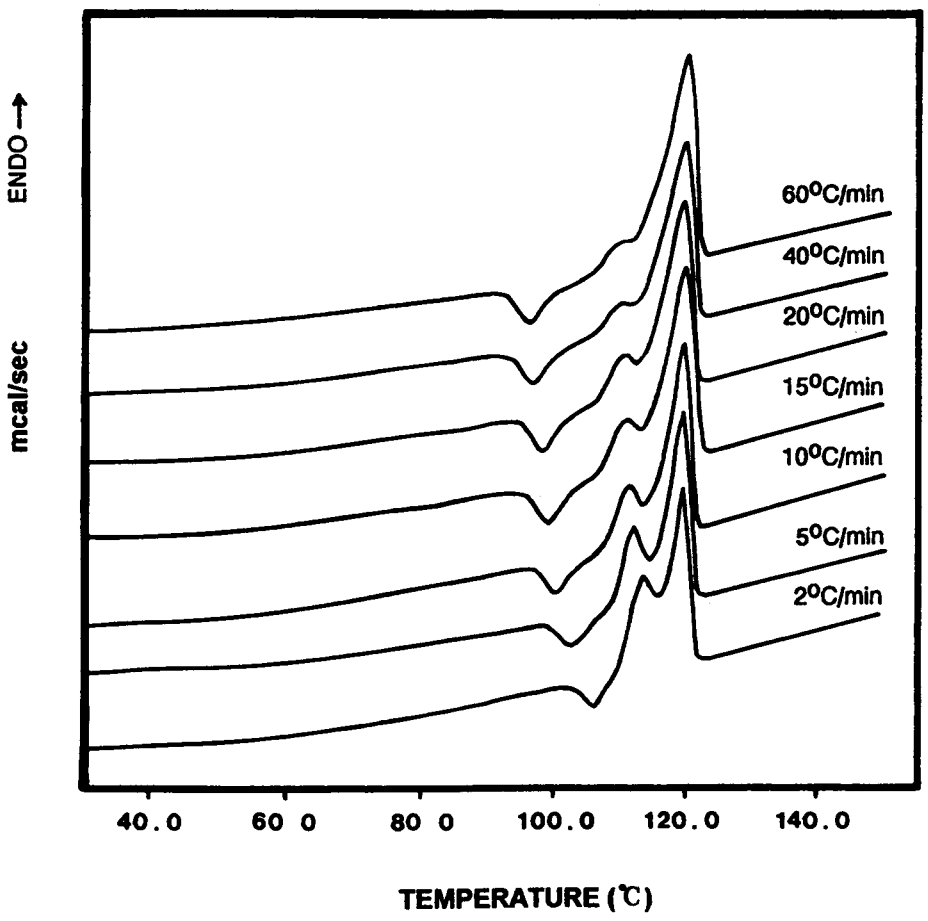

Figure 8 DSC thermograms of poly(1,4-butanediol succinate) (M_w: 18,000) in the reheating process; supercooling processes were accomplished prior to reheating on scan rate 10°C/min.

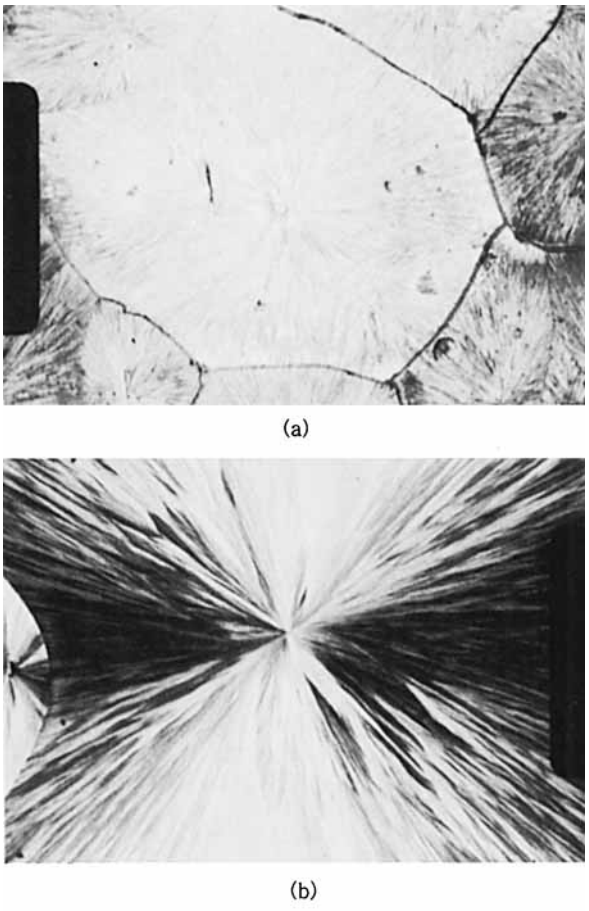

Figure 9 Spherulites grown in the thin film of poly(1,4-butanediol succinate).

Various molecular weights of poly(1,4-butanediol succinate), 4,600, 6,300, 11,000, 18,000, and 29,000 were heated to 150°C at 20°C/min, held for 5 min, and cooled to 30°C at 20°C/min, and then reheated to 150°C. The onset temperature of crystallization and the maximum crystallization temperature were increased with increasing molecular weight to M_w 18,000 (Fig. 5). It is considered that an increase in the onset of crystallization temperature was due to the ease of chain folding in the longer chain. However, in M_w 29,000, the ease of chain folding is limited by the viscosity of the medium. The cold crystallization temperature and melting temperature were increased with increasing molecular weight to M_w 18,000 and decreased in M_w 29,000 (Fig. 6). The increase in the cold crystallization temperature was attributed to a decrease in the number of chain ends, and, subsequently, a loss in the amount of free volume. It is considered that M_w 18,000 has the most perfect crystalline structure among the various molecular weight samples used in this study.

The melt PBS (M_w: 18,000), which was held for 5 min at 150°C, was cooled to 30°C, at various cooling rates, then reheated to 150°C at 10°C/min (Figs. 7 and 8). The onset temperature of crystallization from the melt occurred at lower temperatures as the cooling rate increased and cold crystallization temperature increased with an decreasing cooling rate from the melt. This can be attributed to the effect of slower rates, which allow more time for nucleation, reorganization, and packing of the polymer chains.

Morphology

Figure 9 shows the spherulite structure of PBS that was crystallized from the melt. In the PBS spherulites, a radiating texture can be observed [Fig. 9(a), ×256] and branching texture of the spherulites can be observed clearly [Fig. 9(b), × 512]. The spherulite formed in PBS has a Maltese cross.

Biodegradation

Spherulite of PBS is maintained after sterilization at 140°C for 4 h (Fig. 10). The micrographs of degraded polymer films by micro-organisms are shown in Figure 11 to Figure 18. In the case of sample having M_w of 6,300, the crystalline structure is already degraded by fungi after 1 week, as seen in Figure 11(a) and Figure 12(a). After 3 weeks, some degrade areas are seen where no filament is present. The degradation seen along the mycelia is sufficient to cause the mycelia to sink into the surface of the film after 7 weeks. The degradation of poly(1,4-butanediol succinate) (M_w: 6,300) by actinomycetes and bacteria is similar to the sequence of events observed with the fungi except longer existence of crystalline structure. The degradation trends on poly(1,4-butanediol succinate) (M_w: 29,000) are similar to low molecular weight polymer (M_w: 6,300). But the crystalline structure on M_w 29,000 is maintained longer than M_w 6,300. It is considered that polymer is de-

Table VI Changes of the Molecular Weight of PBS(M_w: 29,000) with Degradation Time by *Aspergillus niger*

Degradation Time (Week)	M_n	M_w	M_w/M_n
0	16,000	29,000	1.82
7	1,600	3,400	2.13
10	700	1,300	1.86

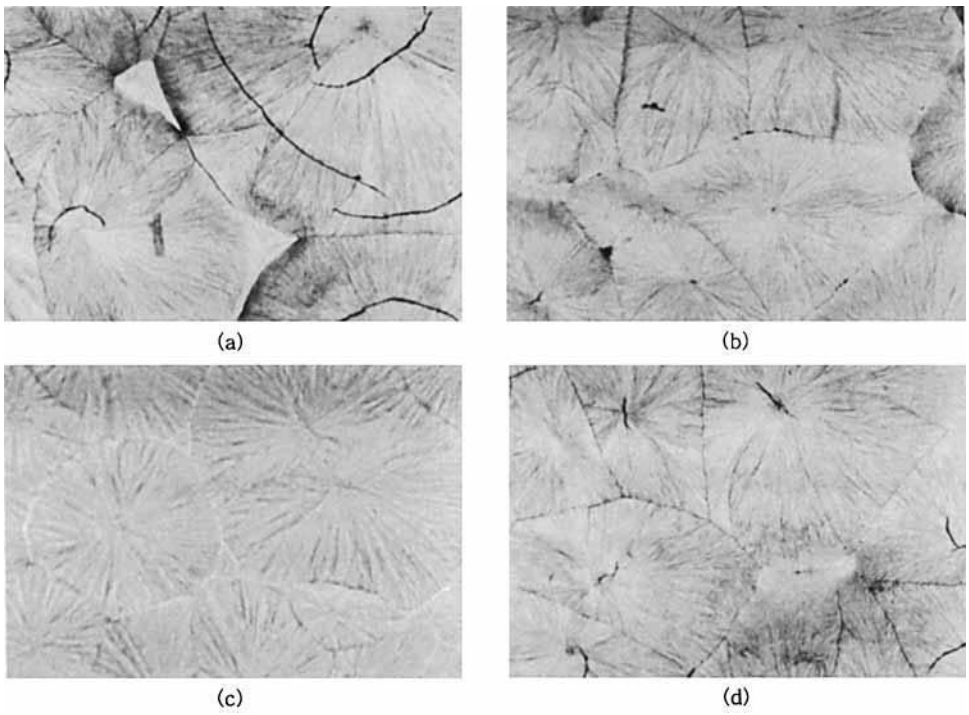

Figure 10 Micrographs of poly(1,4-butanediol succinate) films. Films were sterilized at 140°C for 4 h; (a) M_w 6,300, (b) M_w 29,000. The suspension of microorganism was inoculated on the polymer film; (c) M_w 6,300 (d) M_w 29,000.

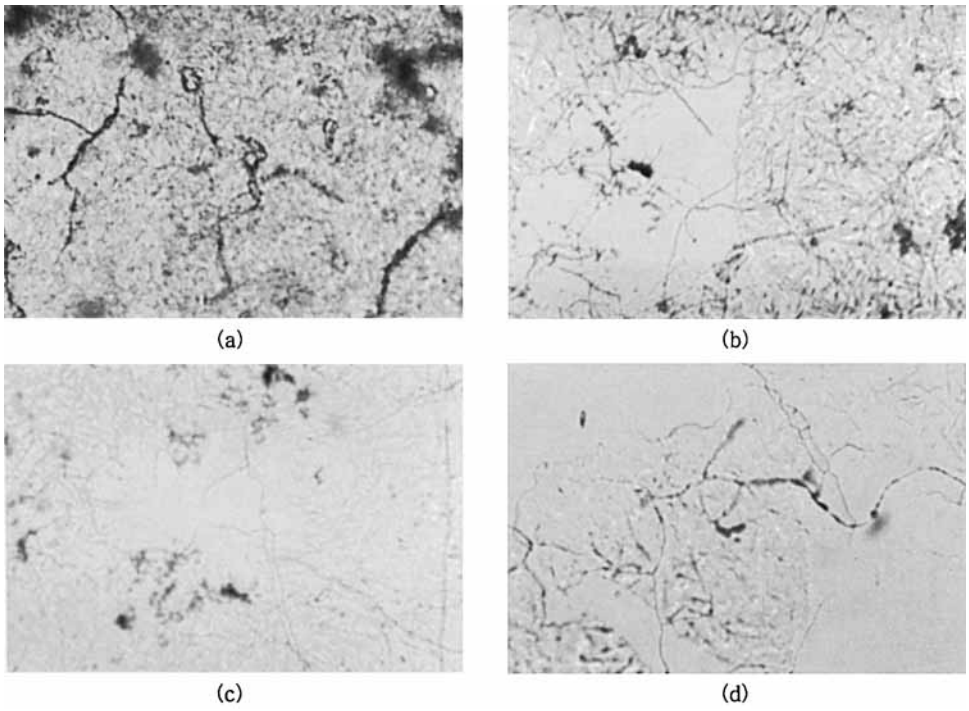

Figure 11 Biodegradation of poly(1,4-butanediol succinate) (M_w: 6,300) by *Aspergillus niger:* (a) 1 week, (b) 3 weeks, (c) 7 weeks, (d) 10 weeks.

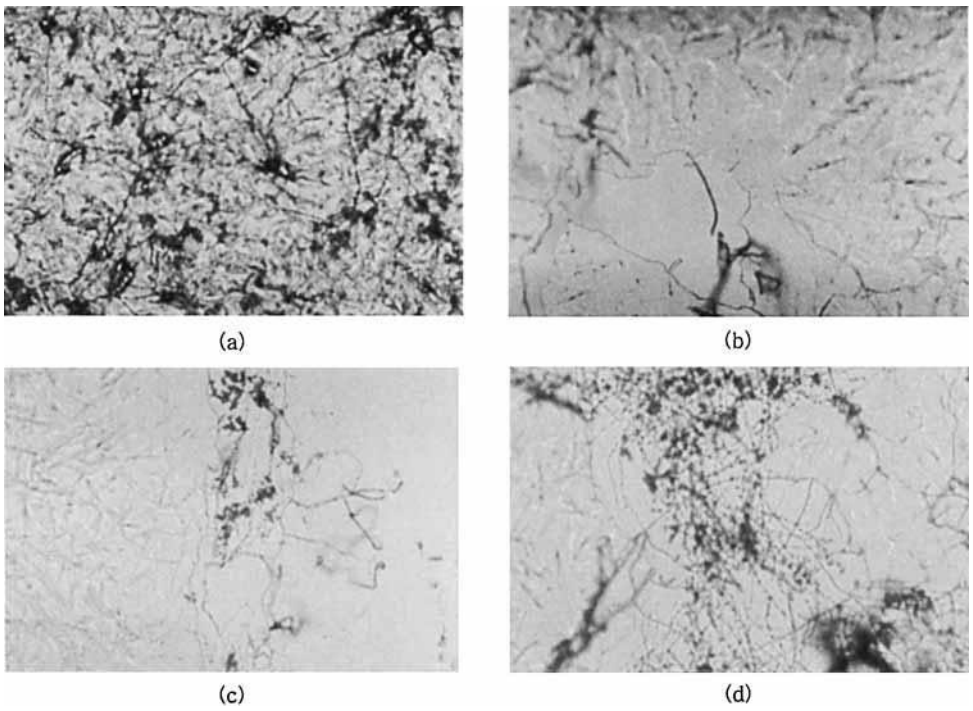

Figure 12 Biodegradation of poly(1,4-butanediol succinate) (M_w: 6,300) by *Penicillium funicularium:* (a) 1 week, (b) 3 weeks, (c) 7 weeks, (d) 10 weeks.

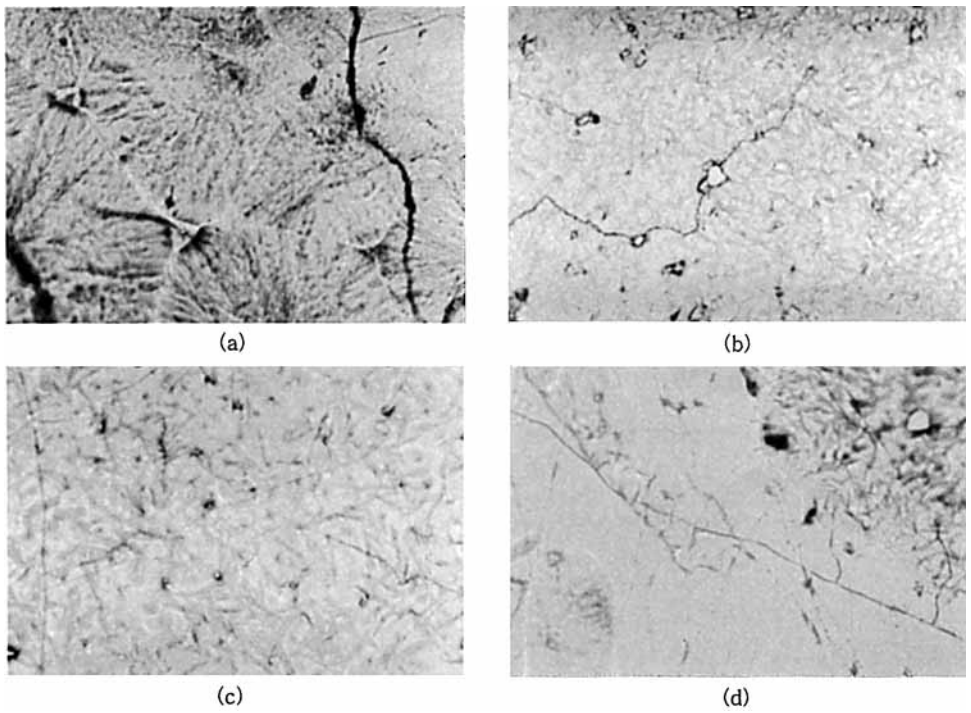

Figure 13 Biodegradation of poly(1,4-butanediol succinate) (M_w: 6,300) by *Actinoplane spp:* (a) 1 week, (b) 3 weeks, (c) 7 weeks, (d) 10 weeks.

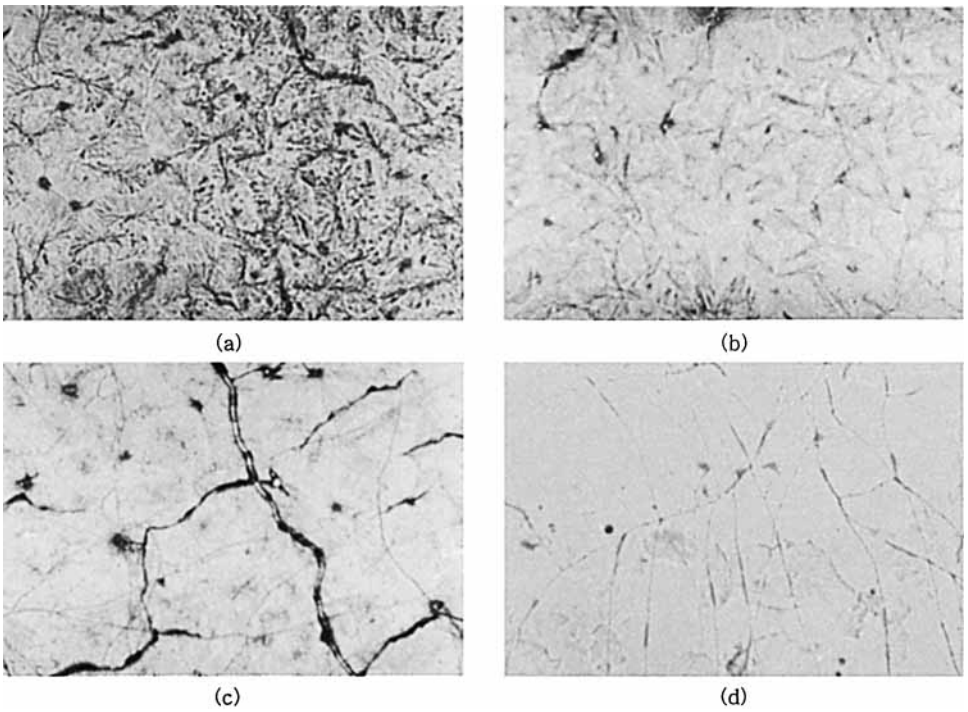

Figure 14 Biodegradation of poly(1,4-butanediol succinate) (M_w: 6,300) by *Pseudomonas fluorescens:* (a) 1 week, (b) 3 weeks, (c) 7 weeks, (d) 10 weeks.

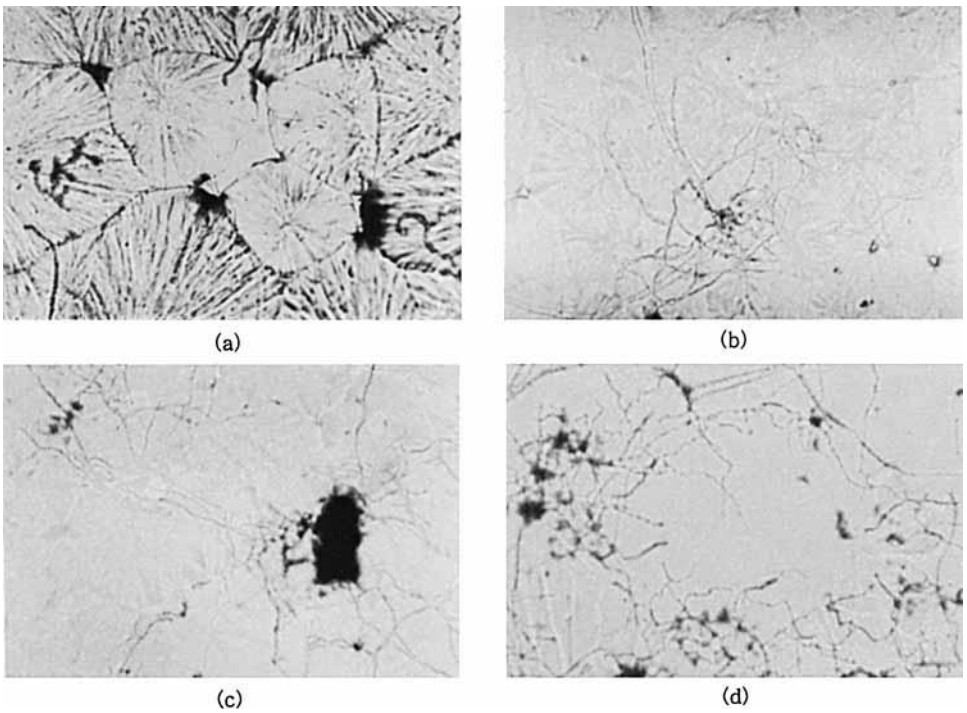

Figure 15 Biodegradation of poly(1,4-butanediol succinate) (M_w: 29,000) by *Aspergillus niger:* (a) 1 week, (b) 3 weeks, (c) 7 weeks, (d) 10 weeks.

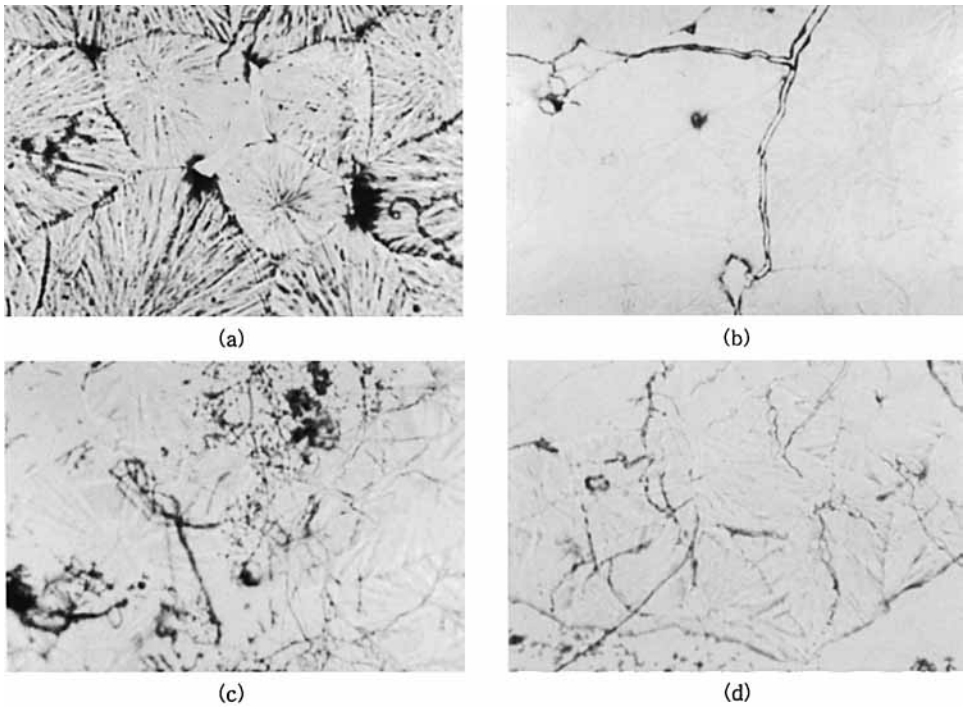

Figure 16 Biodegradation of poly(1,4-butanediol succinate) (M_w: 29,000) by *Penicillium funicularium:* (a) 1 week, (b) 3 weeks, (c) 7 weeks, (d) 10 weeks.

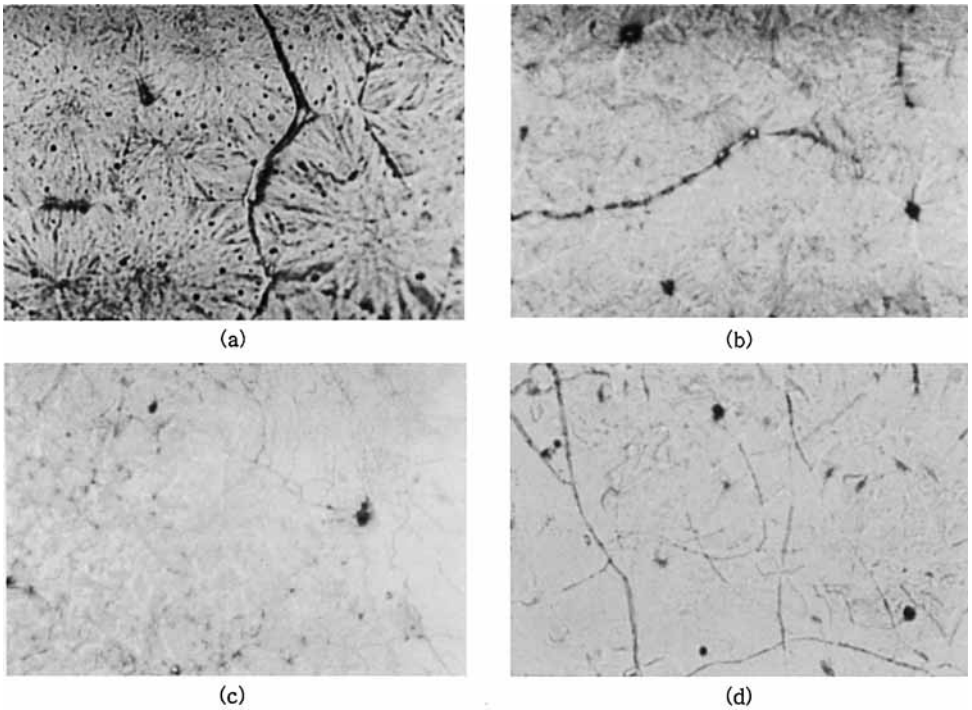

Figure 17 Biodegradation of poly(1,4-butanediol succinate) (M_w: 29,000) by *Actinoplane spp:* (a) 1 week, (b) 3 weeks, (c) 7 weeks, (d) 10 weeks.

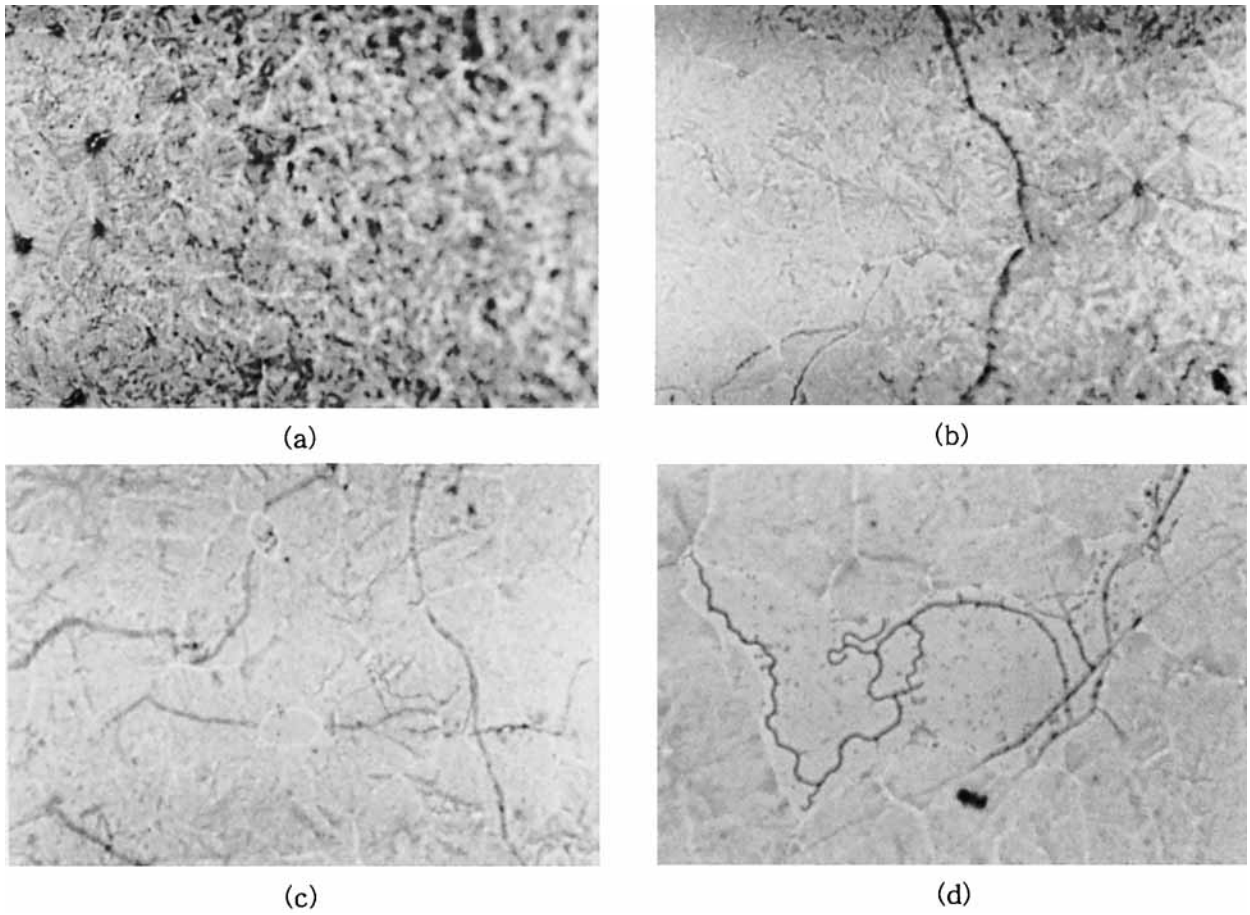

Figure 18 Biodegradation of poly(1,4-butanediol succinate) (M_w: 29,000) by *Pseudomonas fluorescens:* (a) 1 week, (b) 3 weeks, (c) 7 weeks, (d) 10 weeks.

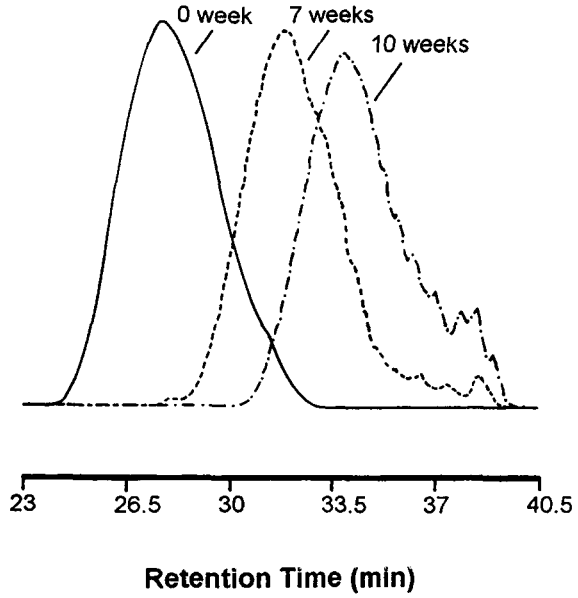

Figure 19 GPC profiles of PBS (M_w: 29,000) before and after biodegradation by *Aspergillus niger.*

graded randomly, but crystalline structure continuously, until reaching very low molecular weight. The ability of *Aspergillus niger* to degrade PBS (M_w: 29,000) was monitored using GPC (Fig. 19). Changes of the molecular weights of PBS are shown in Table VI. As the GPC curves in Figure 19 clearly indicate, the molecular weight of PBS decreased with increasing degradation time. Several peaks, appearing in the low molecular weight region of the GPC curves, are ascribed to oligomeric compounds formed by degradation. The microorganisms studied here are apparently producing an enzyme that is responsible for the biodegradation of the polymer.

CONCLUSIONS

For the preparation of biodegradable polyesters, poly(1,4-butanediol succinate) was synthesized using 1,4-butanediol with succinic anhydride. From the NMR analysis, it was found that the molar ratio of

1,4-butanediol unit to succinyl unit in PBS is 1 : 1. The weight average molecular weights of poly(1,4-butanediol succinate) were between 4,600 and 29,000, and the molecular weight distributions were in the range of 1.7 and 1.9, respectively.

In the DSC study, PBS has a glass transition temperature at 73°C, with multiple melting endotherm. Chain scission and/or crosslinking did not occur in the melt state with various holding times. Slower scanning rates can allow more times for nucleation, reorganization, and packing of the polymer chain, so the onset temperature of crystallization from the melt was increased. M_w 18,000 has more perfect crystalline structure among the various molecular weight samples used in this study. PBS crystallized from the melt was found to have spherulitic structure. In the biodegradation study, PBS was degraded by the microorganisms such as fungi, actinomycetes, and bacteria.

The authors thank the Ministry of Education Research Fund for Advanced Materials in 1993 for the financial support of this work.

REFERENCES

1. X. Zhang, M. F. A. Goosen, U. P. Wyss, and D. Pichora, *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.*, **C33**(1), 81 (1993).
2. M. Vert, F. Ohabot, and P. Christel, *Makromol. Chem. Suppl.*, **5**, 30 (1981).
3. A. S. Hoffmann, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **31**, 313 (1977).
4. S. W. Kim, R. V. Petersen, and J. Feijen, in *Drug Design*, Vol. 6, E. J. Ariens, Ed., Academic Press, New York, 1980, p. 193.
5. R. Langer and N. Peppas, *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.*, **C23**, 61 (1983).
6. K. D. Ahn, I. C. Kwon, and Y. H. Kim, *Polymer (Korea)*, **11**(2), 97 (1987).
7. G. S. Kumar, V. Kalpagam, and U. S. Nandi, *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.*, **C22**(2), 225 (1982–83).
8. P. J. Hocking, *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.*, **C32**, 35 (1992).
9. D. Cohn and H. Younes, *J. Biomed. Mater. Res.*, **22**, 99 (1988).
10. J. M. Mayer and D. L. Kaplan, *Trends Polym. Sci.*, **2**(7), 227 (1994).
11. H. Fukuzaki, M. Yoshida, M. Asano, Y. Aiba, and I. Kaetsu, *Eur. Polym. J.*, **24**(11), 1029 (1988).
12. H. Fukuzaki, Y. Aiba, M. Yoshida, M. Asano, and M. Kumakura, *Makromol. Chem.*, **190**, 2571 (1989).
13. H. Fukuzaki, M. Yoshida, M. Asano, M. Kumakura, K. Imasaka, T. Nagai, T. Mashimo, H. Yuasa, K. Imai, and H. Yamanaka, *Eur. Polym. J.*, **26**(12), 1273 (1990).
14. C. Braud, C. Bunel, H. Garreau, and M. Vert, *Polym. Bull.*, **9**, 198 (1983).
15. A. Carou, C. Braud, C. Bunel, and M. Vert, *Polymer*, **31**, 1797 (1983).
16. T. Ouchi and A. Fujino, *Makromol. Chem.*, **190**, 1523 (1989).
17. T. Ouchi, H. Kobayashi, and T. Bunda, *Br. Polym. J.*, **23**, 221 (1990).
18. American Standards for Testing and Materials, ASTM D G21-70, 1985 *Annual Book of Standards*, American Standards for Testing and Materials, Philadelphia, PA, 1985, p. 1052.
19. Y. K. Han, P. G. Edelman, and S. J. Huang, *J. Makromol. Sci. Chem.*, **A25**(5–7), 847 (1988).
20. J. K. DePorter, D. G. Baird, and G. L. Wilkes, *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.*, **C33**(1), 1 (1993).
21. A. J. Lovinger, F. J. Padden, Jr., and D. D. Davis, *Polymer*, **29**, 229 (1988).
22. A. J. Lovinger and D. D. Davis, *J. Appl. Phys.*, **58**(8), 2843 (1985).
23. D. J. Blundell and B. N. Osborn, *Polymer*, **24**, 953 (1983).
24. W. O. Statton, *J. Appl. Polym. Sci.*, **7**, 803 (1963).
25. G. L. Collins and J. D. Menczel, *Polym. Eng. Sci.*, **32**(17), 1270 (1992).
26. L. C. Lopez and G. L. Wilkes, *Polymer*, **30**, 882 (1989).
27. L. C. Lopez, G. L. Wilkes, and J. F. Geibel, *Polymer*, **30**, 147 (1989).
28. J. D. Hoffman, *Polymer*, **23**, 656 (1982).
29. J. D. Hoffman, I. J. Frolen, G. S. Ross, and J. I. Lauritzen, Jr., *J. Res. Natl. Bur. Stds.*, **79**(A), 671 (1975).
30. M. Inoue, *J. Polym. Sci.*, **55**, 753 (1961).
31. C. J. G. Plummer and H. H. Kausch, *Polymer*, **34**, 305 (1993).
32. R. C. Roberts, *J. Polym. Sci.*, **B**(8), 381 (1970).
33. G. E. Sweet and J. P. Bell, *J. Polym. Sci.*, **A2**(10), 1273 (1972).
34. M. Todoki and T. Kawaguchi, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1067 (1977).
35. J. T. Yeh and J. Runt, *J. Polym. Sci., Polym. Phys.*, **B2**, 1543 (1989).
36. M. E. Nichols and R. E. Robertson, *J. Polym. Sci., Polym. Phys.*, **B**(30), 305 (1992).
37. M. E. Nichols and R. E. Robertson, *J. Polym. Sci. Polym. Phys.*, **B**(30), 755 (1992).

Received June 5, 1994
Accepted November 3, 1994