

Synthesis and Characterization of Biodegradable Poly(butylene succinate)-*co*-oligo(L-valine) Copolyesters via Direct Melt Transesterification

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ABSTRACT: A series of aliphatic biodegradable poly(butylene succinate)-*co*-oligo(L-valine) (PBSVAL) copolyesters were synthesized with dimethyl succinate, 1,4-butanediol (BDO), and oligo(L-valine) (OVL) as reagents. The GPC results show that the weight average molecular weight (M_w) of the copolyester with a feed ratio (PBS/OVL) of 0.9/0.1 (PBSVAL₁₀) is 4.9×10^4 g/mol, and its polydispersity index is 1.68. All the copolyesters were more thermally stable than the pristine poly(butylene succinate) (PBS). The incorporation of valine units into the copolyesters eventually led to the decrease of the crystallization temperature, melting temperature, while increase of crystallization enthalpy and melting enthalpy. The crystal

structure of the copolyesters is similar to pure PBS except for higher degrees of crystallinity; also there was a trend to higher degrees of crystallinity with increasing content of valine. From the enzymatic degradation experiment, it is clear that the PBSVAL₁₀ copolyester shows less weight loss as compared to pure PBS which is due to PBSVAL₁₀ with higher degree of crystallinity. The morphology of the copolyester films after degradation was also studied by the scanning electron microscopy. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 3092–3099, 2012

Key words: poly(butylene succinate); copolyesters; crystallization; biodegradation

INTRODUCTION

In the past two or three decades, there has been considerable interest in the development of biodegradable and biocompatible polymers. Among the synthetic biodegradable polymers, aliphatic polyesters, poly(butylene succinate) (PBS),¹ polylactide (PLA),² and Poly(amino acid)^{3,4} have been thoroughly investigated and use in the field of pharmaceutical, agricultural, and biomedical materials.^{5–7}

PBS is a kind of biodegradable aliphatic polyesters that is used in a wide range of engineering applications. Because of its excellent properties, such as safety and nontoxicity regarding any health related issues,⁸ good mechanical properties when compared with other degradable polyesters. Many investigations about PBS have been carried out both in theories and applications. However, the insufficient properties of PBS, especially incompatibility, poor

mechanical property, and high crystallinity have limited its application seriously, and so various methods have been explored to overcome these weaknesses. An efficient method of modifying the properties of PBS is to prepare its copolymers, such as poly(butylene succinate-*co*-butylene adipate)(PBSA), its mechanical properties similar to polyolefin.⁹ Up to now, many studies on the synthesis, characterization, degradation, crystallization, and other properties of PBS and its copolyesters have been reported^{10–12}; however, to the best of our knowledge, there were few reports about the synthesis or properties of PBS-*co*-(amino acids).

Introduction of amino acids into the polymer chain of PBS is an efficient route for improving the characters of PBS. Amino acids are essential to biological function such as biodegradable, biocompatible, and can be used to develop synthetic biodegradable or bioactive polymers, which can be used in medical, cosmetic, fabric, and metal absorbent materials.¹³ On the other hand, amino acid-based aliphatic polyesters^{14–22} are important biodegradable polymers, and have attracted much attention from both academic and industrial scientists.²³ For example, poly-L-lysine with controlled low-molecular weight was synthesized and characterized by Wendelmoed and van Dijk-Wolthuisa,²⁴ also biodegradable poly(lactic acid-*co*-glycine) [P(LA-*co*-Gly)]²⁵ was

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used as biomedical material. Furthermore, increasing emphasis has been given to the applications of Gly-modified PLA in drug-delivery systems.²⁶

Functionalized amino-acid-based PBS constitute a promising family of biodegradable materials since they combine a degradable character, afforded by hydrolyzable ester groups (—COO—) in the backbone, with relatively good thermal and mechanical properties given by the strong intermolecular hydrogen bonding interactions that can be established between their amide groups (—NHCO—). This material will have excellent processability, biodegradability, biocompatibility, and nontoxic properties. In this study, aliphatic biodegradable poly(butylene succinate)-*co*-oligo(L-valine) (PBSVAL) copolyesters were synthesized and characterized, which combines the characters of PBS and amine acids, and would produce a new family of polymeric materials. On the basis of successful synthesis of PBS copolymers, the relationships between composition and thermal, mechanical, and enzymatic degradation behaviors of copolyesters were established.

EXPERIMENTAL

Materials

Dimethyl succinate (DMS) was purchased from Alfa Aesar (Tianjin, China). 1,4-butanediol (BDO) was purchased from Sinopharm Chemical Reagent (Shanghai, China). L-valine and SnO were purchased from Aladdin Reagent Database (Shanghai, China). All the reagents were used as received without further purification.

Synthesis of oligo(L-valine)

Oligo(L-valine) (OLV) was synthesized by the following procedure (Scheme 1). Briefly, 20 g of L-valine (Fluka) was dissolved in 30 mL of formic acid, then added 0.02 g SnO as the catalyst, heated stepwise to 150°C and kept at this temperature for 4 h. The corresponding weight-average molecular weight (\overline{M}_w),

number-average molecular weight (\overline{M}_n), and the polydispersity index (PDI) ($\overline{M}_w/\overline{M}_n$) of OVL measured by the gel permeation chromatography (GPC): $\overline{M}_n = 2000$ g/mol, $\overline{M}_w = 3500$ g/mol, and $\overline{M}_w/\overline{M}_n = 1.75$.

Synthesis of copolyesters

The aliphatic copolyesters PBSVAL were synthesized by melt transesterification method with DMS, BDO, and OVL as reagents, and the reaction route is shown in Scheme 1(b). The valine units were introduced into the PBS chains by transesterification. DMS, BDO, OVL, and Ti(OBu)₄ (0.1 mol% of the total chemicals) were placed into a 250 mL three-neck glass reactor equipped with a condenser, nitrogen inlet and outlet, a central mechanical stirrer. At the beginning, the reactor was placed in an oil bath, and then quickly heated to 180°C and kept for 2 h under this temperature. After that, the reaction system was gradually heated up to 230°C and kept for 3 h under nitrogen atmosphere. And then, the reaction continued for another 3 h under a vacuum of 50 Pa. Finally, the reaction system was cooled to room temperature under nitrogen, and then, the synthesized polyester was dissolved in 50 mL of chloroform, followed by the precipitation into 500 mL of methanol. The product was collected by filtration and then dried under vacuum at 40°C for 2 days.

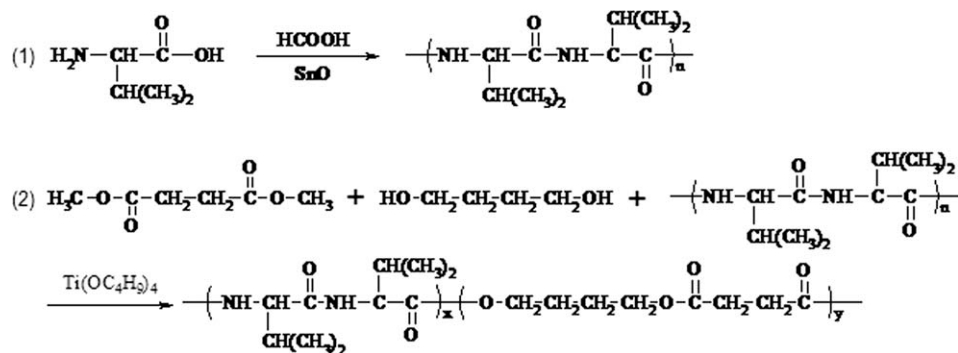
Characterization

Gel permeation chromatography

The GPC was conducted with a Breeze Waters system using polystyrenes as the standard and chloroform as the eluent at a flow rate of 1.0 mL/min.

Nuclear magnetic resonance (NMR) spectroscopy

To investigate the composition of PBSVAL copolyesters, ¹H-NMR measurement was carried out at room temperature using a Bruker ARX spectrometer operated at a resonance frequency of 600 NMR. The copolyesters were dissolved in deuterated



Scheme 1 Synthesis route of oligo(L-valine) (OVL) and PBSVAL copolyester.

chloroform (CDCl_3), and tetramethylsilane ($\delta = 0$) was used as the internal standard of chemical shift in NMR spectrum, and the measurement parameters including the amount of scans, acquisition time and pulse width were 64, 9.04, and 23, respectively.

Different scanning calorimeter

Different scanning calorimeter (DSC) measurements of copolyesters were carried out on a differential scanning calorimeter (Shimadzu DSC-60) under a nitrogen flow at a rate of 20 mL/min. The samples of about 5 mg were heated quickly to 150°C and held for 5 min to erase thermal history. Then, the samples were cooled to -50°C and reheated to 150°C at a rate of 10°C/min. The glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), melting enthalpy (ΔH_m), and crystallization enthalpy (ΔH_c) were recorded.

Wide angle X-ray diffraction

Wide angle X-ray diffraction (WAXD) experiments were used to analyze crystalline structure of the samples by a Bruker D8 Focus X-ray diffractometer, operating at 30 kV and 20 mA, with a copper target of $\lambda = 0.154$ nm. The patterns in the range of 5°–45° (2 θ) were obtained at a scanning rate of 1°/min.

Polarized optical microscopy

Polarized optical microscopy (POM) was carried out with a Nikon E600POL microscope in conjunction with a hot stage (Instec HS 400). The samples were first heated to 150°C on a hot plate holding for 5 min and then quenched to the required crystallization temperature. The growth of spherulites was recorded on a video cassette recorder.

Mechanical properties

Mechanical properties were determined by a SANS WDW universal system with electronic data evaluation on specimen of 70 × 25 mm² with a thickness in the range of 0.04–0.06 mm determined by a vernier caliper. The specimens were cut from melt-pressed films by a mold equipped with knives. At least five specimens were tested for each sample and the average values were obtained.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on a PerkinElmer TGA 7 at a heating rate of 20°C/min under nitrogen atmosphere with a sample size of 8–10 mg.

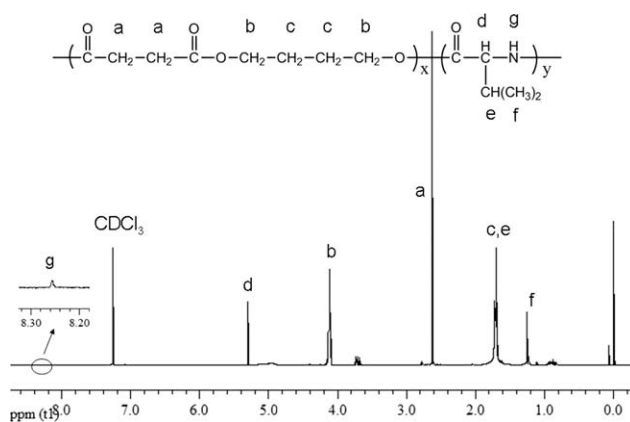


Figure 1 $^1\text{H-NMR}$ spectrum of the PBSVAL₁₀ copolyester.

Enzymatic degradation

The copolyesters films (50 × 20 × 0.06 mm³) prepared by melt-pressed were placed in vials containing 8 mL of phosphate buffer solution (pH 7.4 at 25°C) with 5.0 mg/mL *Pseudomonas cepacia* lipase at constant temperature of 37°C. At predetermined degradation time intervals, the specimens were removed from the medium, rinsed with distilled water, dried under vacuum at room temperature for one week and weighed. Weight loss percentages of the copolyesters were obtained according to the relationship:

$$\text{Weight loss (\%)} = (W_0 - W_r)/W_0 \times 100\% \quad (1)$$

where W_0 is the initial weight and W_r is the dry weight of the specimens after degradation.

The surfaces of degraded samples after the enzymatic degradation for different time intervals were observed with SEM (Quanta 200 F).

RESULTS AND DISCUSSION

Structure of copolyesters

The PBSVAL copolyesters were synthesized via the two-stage polycondensation process as shown in Scheme 1. In the copolyesters, the "BS" in the sample code represents for the butylene succinate unit, and "VAL" represents for OLV. The chemical structure is one of the key points determining the properties of the copolyesters. The molecular structure of the PBSVAL copolyester was investigated by $^1\text{H-NMR}$ spectroscopy. Figure 1 shows the $^1\text{H-NMR}$ spectrum for PBSVAL₁₀ copolyester with molar feed ratio PBS/VAL = 90/10. The peak at 2.63 ppm (proton a) is assigned to protons from the CH_2 of succinate. And the signals occurring at 4.17 ppm (proton b) and 1.72 ppm (proton c) could be reasonably assigned to the outer and inner protons of CH_2 of ethyleneoxide unit, respectively. Furthermore, the

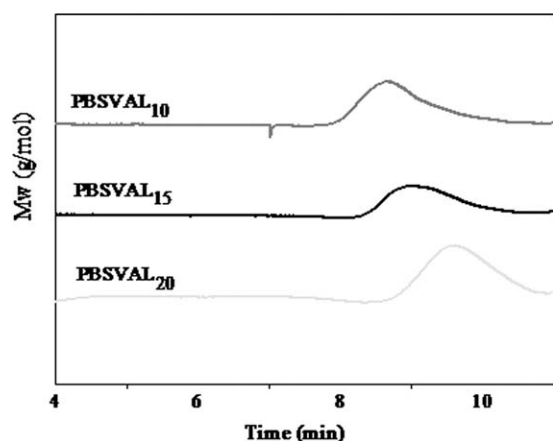


Figure 2 GPC curves of PBSVAL₁₀, PBSVAL₁₅, and PBSVAL₂₀ copolyesters, respectively.

peaks at 5.16 ppm (proton d), 1.71 ppm (proton e), 1.26 ppm (proton f), and 8.25 ppm (proton g) are attributed to protons from the CH linking to carbonyl, CH linking to methyl group, and CH₃, respectively. From these results, it can be indicated that the BS and VAL units were formed in the backbone of copolyester.

For the molecular weight determination and molecular weight distribution of the copolymers, the GPC curve of PBSVAL10 was obtained and showed only a single peak, as shown in Figure 2. The weight-average molecular weight was 4.9×10^4 g/mol, number-average molecular weight was 2.9×10^4 g/mol, and the PDI was 1.68. The monomodal peak and low PDI (less than 2) indicated that the product from two monomers is indeed a copolymer, and not a mixture containing any homopolymer, PBS or OLV.

Thermal properties of copolyesters

The thermal stabilities of PBS and its copolyesters were studied using TGA, as shown in Figure 3. Because of the incorporation of valine units, all the copolyesters were more thermally stable than the pristine PBS.

The synthesized copolyesters were partly crystalline polymers, for which melting and crystallization temperatures were observed by DSC analysis. The DSC thermograms of the copolyesters recorded during cooling and heating that are presented in Figure 4(a,b), respectively. The melting of the crystallites of the PBS and copolyesters occurs in the temperature region 104–106°C, while crystallization occurs in the range of 55–78°C. The DSC thermograms illustrate a significant shift of the melting temperatures to lower temperatures with increasing valine contents in copolyesters, also the same to the crystallization temperatures.

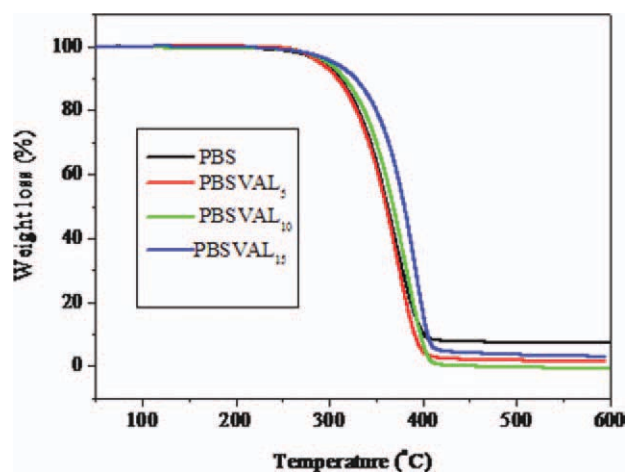


Figure 3 TGA curves of PBS, PBSVAL₅, PBSVAL₁₀, and PBSVAL₁₅ for 1.5 h, respectively (heating rate of 20°C/min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The results obtained from DSC analysis, the corresponding melting temperature (T_m), crystallization temperature (T_c), melting enthalpy (ΔH_m), and as well as crystallization enthalpy (ΔH_c) are illustrated

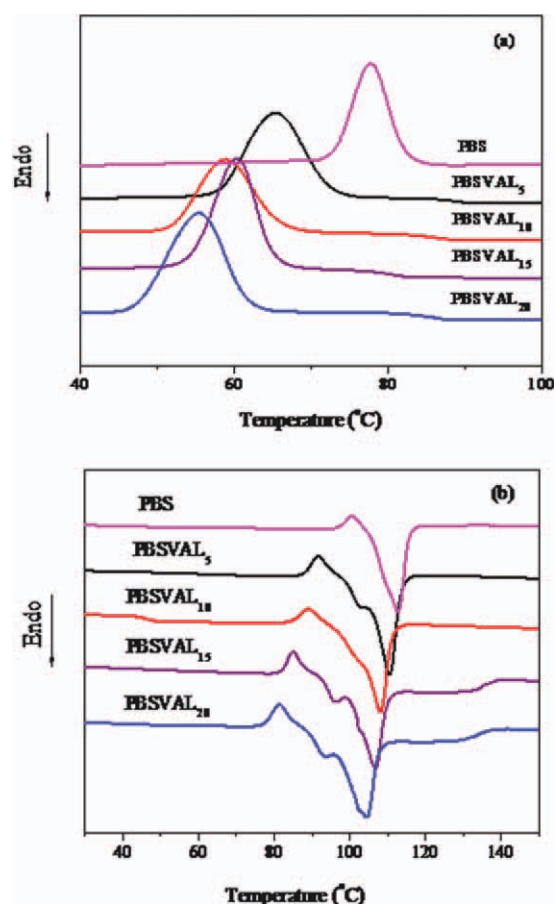


Figure 4 DSC curves of PBS and copolyesters: (a) cooling and (b) second heating. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Thermal Properties and Degrees of Crystallinity for PBS and Copolyesters

Sample	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	X_{C-DSC} (%)
PBS	112.9	60.3	77.9	54.5	54.6
PBSVAL ₅	110.6	64.7	65.4	58.8	59.4
PBSVAL ₁₀	108.2	65.2	59.5	59.0	63.7
PBSVAL ₁₅	106.9	67.12	60.4	59.4	68.2
PBSVAL ₂₀	104.6	73.7	55.5	65.9	80.2

in Table I. Random copolymerization usually results in a decreased melting point, degree of crystallinity, heat distortion temperature, and tensile strength. On the other hand, the elongation at break and impact strength usually rise with copolymerization.²⁷ But in Figure 4, the crystallization peaks shift to lower temperatures, on the contrary, the melting enthalpy (ΔH_m), as well as crystallization enthalpy (ΔH_c) increasing with the valine content increasing for the copolyesters. It was different with other materials. The crystallization temperature as well as melting temperature decreased as the valine units content increased.

As reported, the theoretical value of the melting enthalpy of 100% crystallized PBS homopolymer was determined to be 110.5 J/g, which was calculated on the basis of the group contribution method.²⁸ The total degrees of crystallinity of the copolyesters (X_{C-DSC}) were in the range 54.6–80.2%, which were higher than the degree of crystallinity of the homopolymer PBS, and increased with increasing content of valine. The values of X_{C-DSC} tended to increase with the increasing of valine content, from which it can be included that the presence of the valine units was benefit to the crystal growth of the PBS segments.

Crystal structure of copolyesters

To illustrate the relationship between chemical composition and the crystallization behavior of the copolyesters, it is important to discuss the crystal structure of the copolyesters. Further information on the crystalline structure and degrees of crystallinity of the synthesized copolyesters was obtained from WAXD (as show in Fig. 5). Characteristic peaks for PBS and copolyesters appear at $2\theta = 19.5^\circ$ and 22.6° . The WAXD pattern of PBS homopolymer exhibit a well-defined set of crystalline diffraction peaks, attributable to the alpha phase²⁹: the profile is characterized by two intense reflections at 19.6° and 22.5° , and by some weak reflections between 25° and 45° .³⁰ All the PBSVAL copolyesters show similar diffraction peaks with pristine PBS, proving that the crystal structure that develops in the copolyesters is similar

to pristine PBS. It suggests that PBSVAL copolyesters have the same crystal structure with that of PBS and could be able to crystallize in the PBS cells. However, the positions of the reflection peaks for copolyesters are lower than those of PBS. With the increasing of valine content, the intensity of the peaks at $2\theta = 19.5^\circ$ and 24.6° increased, suggesting that the incorporation of VAL units have no affection on the crystal form; however, the lattice parameters of the PBS has changed. It is also concluded that the valine units have been incorporated into the PBS crystals after the crystallization.³¹ The increase of valine content leads to the formation of crystals with different lattice parameters, which might finally influence the degradation behavior of the copolyesters. Furthermore, the degree of crystallinity for the copolyesters was increased as compared to pure PBS and there was a trend to higher degrees of crystallinity with increasing content of valine.

Crystallization morphology of copolyesters

The differences in spherulite morphology may eventually lead to the change of mechanical and degradable properties. The POM was used to investigate the crystalline morphology of the copolyesters. Figure 6 shows a series of POM micrographs for PBSVAL₁₀ spherulites isothermally crystallized at various temperatures. All micrographs display the typical Maltese crosses. Besides the normal extinction crosses, the banded spherulites with concentric extinction are found in polymer crystallization, it is generally believed that the formation of banded spherulites is attributed to the regular twisting of radial crystallite ribbons.³² The banded spherulites are clearer when the crystallization temperature is

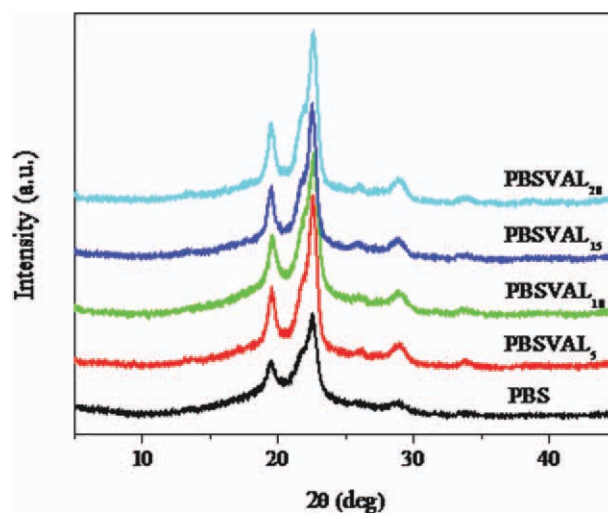


Figure 5 WAXD patterns of PBS and copolyesters. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

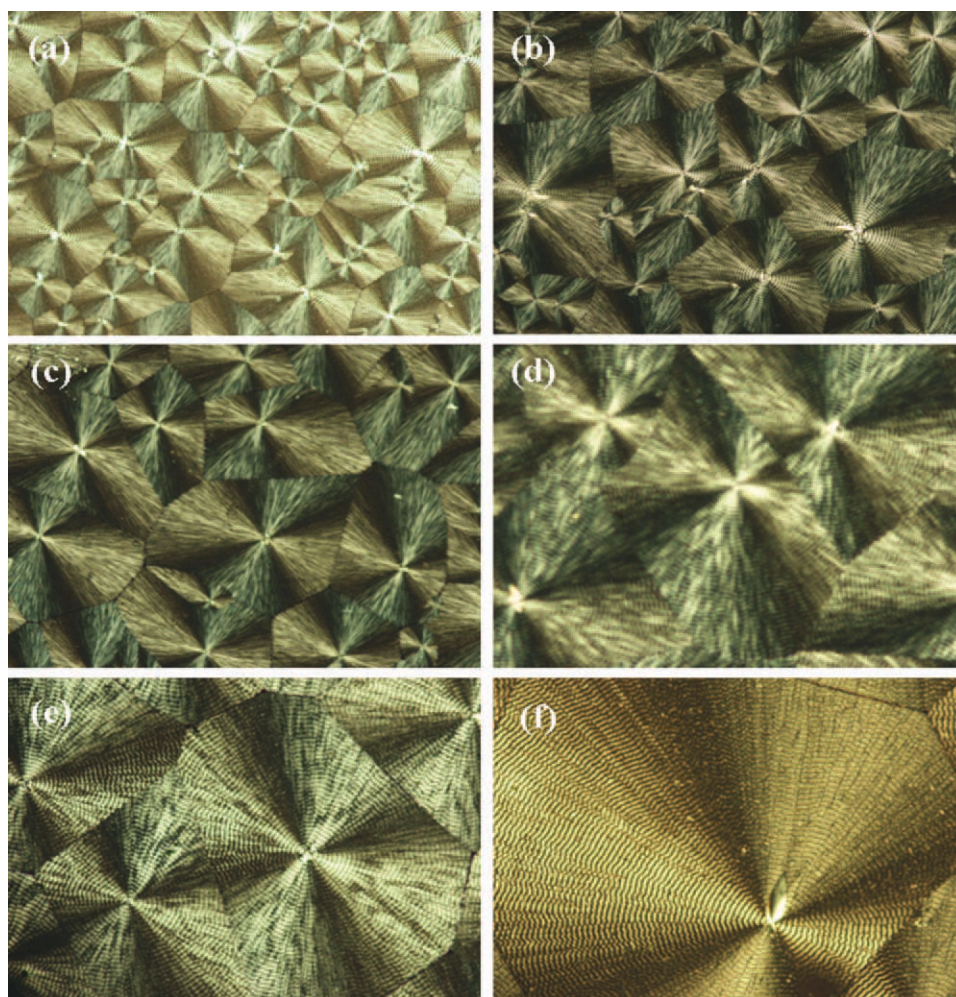


Figure 6 POM graphs for PBSVAL₁₀ after isothermally crystallized at different temperatures for 0.5 h. (a) 55°C, (b) 60°C, (c) 65°C, (d) 70°C, (e) 75°C, and (f) 80°C (The magnitude is 200). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

higher, in addition, with the increase in crystallization temperature the corresponding spherulites size increased in the same order.

Mechanical properties of copolyesters

It is generally accepted that the mechanical properties of the polymers are greatly influenced by the chemical composition, sequential structure, crystal forms, and the degree of crystallinity. On the basis of the above results, it is concluded that the incorporation of VAL units into the copolyesters show significant effect on the crystallization and melting behaviors, the crystal structure and spherulites morphology of the copolyesters. And in order to investigate the relationship between the sequential structure mentioned earlier and the resulting properties of the copolyesters, the mechanical properties of the synthesized polymers PBS and PBSVAL₁₀ are summarized in Table II. As shown in Table II, tensile strength and elongation at break of the PBSVAL₁₀

copolyester are lower than that of pristine PBS; however, the modulus of PBSVAL₁₀ is higher than that of PBS. It indicates that the incorporation of the valine units into the copolyesters, eventually leads to the decrease of tensile strength, elongation at break while increase of tensile modulus.

Enzymatic degradation of copolyesters

In this study, enzymatic degradation is expressed as the percentage of weight loss, and the lipase of *Pseudomonas cepacia* was utilized for analyzing the enzymatic degradation of copolyesters at constant

TABLE II
Mechanical Properties of PBS and Copolyesters

Sample	Tensile strength (MPa)	Elongation (%)	Modulus (MPa)
PBS	29.1	11.1	296.3
PBS ₉₀ VAL ₁₀	19.2	7.1	451.8

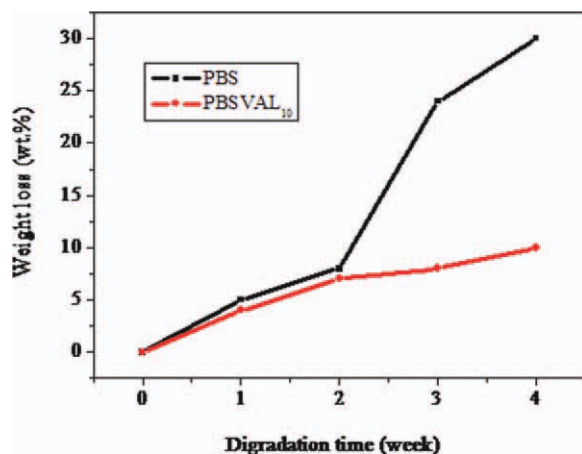


Figure 7 Weight loss versus time during enzymatic degradation for PBS and PBSVAL₁₀, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperature of 37°C. The weight loss of the PBS homopolymer and the PBSVAL₁₀ copolymer during enzymatic degradation process is presented in Figure 7. It is clear that the PBSVAL₁₀ copolymer

shows less weight loss when compared to PBS, because of higher degree of crystallinity. It is suggested that the degradation rate of the copolymer decreased with the addition of valine units. The biodegradation process of the copolymer was also confirmed by SEM microscopy. Figure 8 shows the SEM of the surfaces of PBSVAL₁₀ films after enzymatic degradation of different time. After one week, the surface morphology of PBSVAL₁₀ has handful of holes, cracks, and irregularities after degradation. However, partial regions remained relatively smooth. Besides, many round eroded regions formed. After two weeks, the round regions evolved into holes, also the number of the holes increased and some of them joined together to form large hollow regions. The surface roughened and the holes spread throughout all regions three weeks later. The whole film had almost disintegrated to small fragments and dispersed into the whole films. It indicated that majority of the film had been degraded after three weeks. Four weeks later, a rough surface with large holes, which extend to a large depth formed on the copolymer film. These results

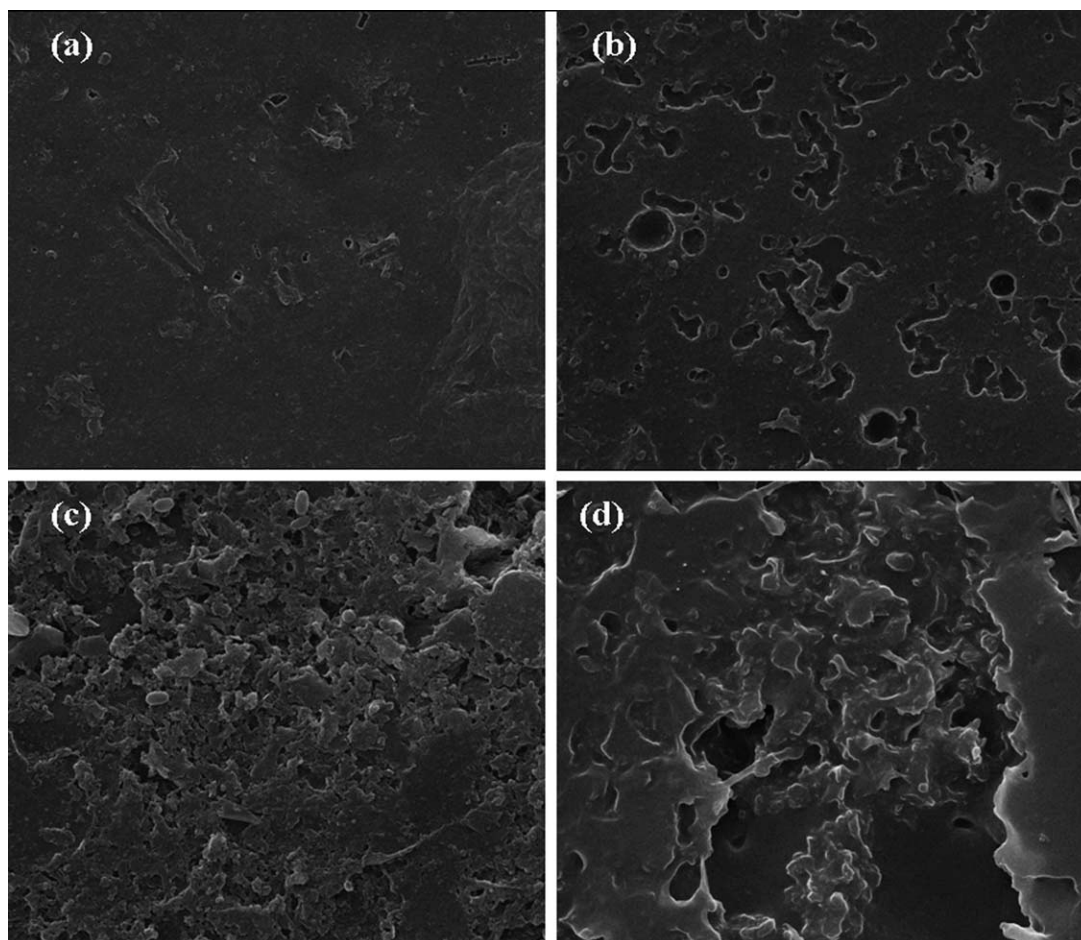


Figure 8 SEM graphs of the surface of PBSVAL₁₀ film after enzymatic degradation for different time intervals. (a) 1 week, (b) 2 weeks, (c) 3 weeks, and (d) 4 weeks, respectively.

suggest that the degradation of the PBSVAL₁₀ began from the surface of films.

CONCLUSIONS

A series of aliphatic biodegradable PBSVAL copolyesters were synthesized with the catalyst of Ti(OBu)₄. The incorporation of valine units into the copolyesters eventually led to the decrease of the crystallization temperature, melting temperature, while increase of crystallization enthalpy and melting enthalpy. The crystal structure of the copolyesters is similar to pure PBS except for higher degrees of crystallinity; also there was a trend to higher degrees of crystallinity with increasing content of valine. The enzymatic degradation test indicates that the PBSVAL₁₀ copolyester show less weight loss because of higher degree of crystallinity when compared to PBS. In addition, mechanical properties of copolyester indicates that the incorporation of the valine units into the copolyesters, eventually leads to the decrease of tensile strength and elongation at break while increase of modulus. The synthesized copolyesters may combine the advantages of PBS and amino acid, such as good degradability, relatively good thermal properties, as well as satisfied mechanical properties, which would become a new family of polymeric materials with potential applications in many fields.

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