

# Blends of Aliphatic Polyesters. IV. Morphology, Swelling Behavior, and Surface and Bulk Properties of Blends from Hydrophobic Poly(L-lactide) and Hydrophilic Poly(vinyl alcohol)

HIDETO TSUJI, HIROKI MURAMATSU

Department of Ecological Engineering, Toyohashi University of Technology, Tempaku-Cho, Toyohashi, Aichi 441-8580, Japan

Received 28 February 2000; accepted 29 August 2000

**ABSTRACT:** Blend films were prepared from hydrophobic poly(L-lactide) (PLLA) and hydrophilic poly(vinyl alcohol) (PVA) with different PLLA contents [ $X_{\text{PLLA}}$  (w/w) = PLLA/(PVA + PLLA)] by solution casting and melt quenching. Their morphology, swelling behavior, and surface and bulk properties were investigated. Polarizing optical microscopy, scanning electron microscopy, differential scanning calorimetry, X-ray diffractometry, and tensile testing revealed that PLLA and PVA were phase separated in these blend films and the PLLA-rich and PVA-rich phases both formed a continuous domain in the blend film of  $X_{\text{PLLA}} = 0.5$ . The water absorption of the blend films was higher for the blend films of low  $X_{\text{PLLA}}$  values when compared at the same immersion time, and it was larger than expected from those of nonblended PLLA and PVA films. The dynamic contact angles of the blend films were linearly increased with an increase in  $X_{\text{PLLA}}$ . The tensile strength and Young's modulus of the dry blend films decreased with a rise in  $X_{\text{PLLA}}$ , but this dependence was reversed because of the large decreases in tensile strength and Young's modulus for the blend films having high  $X_{\text{PLLA}}$  values after immersion in water. The elongation at break was higher for the wet blend film than for the dry blend film when compared at the same  $X_{\text{PLLA}}$  and that of the dry and wet blend films decreased with an increase in  $X_{\text{PLLA}}$ . © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2151–2160, 2001

**Key words:** polylactide; poly(vinyl alcohol); polymer blends; physical properties; swelling behavior

## INTRODUCTION

Recently, there were numerous studies performed on biodegradable polymer blends from hydrophobic polylactides (PLAs) and their copolymers with

hydrophilic polymers to determine their biomedical, pharmaceutical, and ecological applications.<sup>1–6</sup> The purposes of these works are divided into two groups: the preparation of biodegradable materials having a wide variety of mechanical and swelling properties,<sup>1–4</sup> drug delivery profiles,<sup>1,4</sup> and enzymatic<sup>3</sup> and nonenzymatic<sup>1,2,4</sup> hydrolyzability; and the preparation of porous biodegradable scaffolds for tissue reconstruction.<sup>5–7</sup> The hydrophilic biodegradable polymers utilized so far include poly(vinyl alcohol) (PVA),<sup>1</sup> poly(eth-

Correspondence to: H. Tsuji (tsuji@eco.tut.ac.jp).

Contract grant sponsor: Ministry of Education, Culture, Sports, Science and Technology, Japan; contract grant number: 11217209.

*Journal of Applied Polymer Science*, Vol. 81, 2151–2160 (2001)  
© 2001 John Wiley & Sons, Inc.

ylene oxide) (PEO),<sup>2,3,6</sup> and an A–B–A type triblock copolymer from PEO (A), poly(propylene oxide) (B, Pluronic),<sup>4</sup> and gelatin.<sup>5</sup> The water solubility of the hydrophilic polymers depends on their molecular structure and molecular weight. Hydrophilic water-insoluble and water-soluble polymers were utilized for the former and the latter purposes, respectively.

Pitt et al. reported that the hydrolysis rate, water content, and permeability coefficient of the blends from (50/50) poly(DL-lactide-co-glycolide) [P(DLLA-GA)] and water-insoluble PVA increased with a rise in PVA content; they concluded that P(DLLA-GA) and PVA were miscible when the P(DLLA-GA) content was smaller than 30 wt %.<sup>1</sup> Nijenhuis et al. studied the change in the mechanical and swelling properties of poly(L-lactide) (PLLA) upon the addition of a small amount of water-soluble PEO up to 20 wt %.<sup>2</sup> Park et al. demonstrated that PLLA and Pluronic were partially miscible and the addition of Pluronic to a drug delivery PLLA matrix extended its protein release and minimized its initial protein burst compared with the pure PLLA matrix.<sup>4</sup> Recently, Sheth et al. found that the weight loss rate of PLLA by enzymatic hydrolysis was significantly increased by the addition of a small amount of water-soluble PEO.<sup>3</sup>

Thomson et al. prepared the porous P(DLLA-GA) materials having different pore sizes by extraction of water-soluble gelatin particles with different particle sizes from their blends.<sup>5</sup> We prepared porous PLLA<sup>6</sup> or poly( $\epsilon$ -caprolactone) (PCL)<sup>7</sup> materials by extraction of water-soluble PEO from their blends and found that their porosity and pore size could be altered by varying their blending ratio and the molecular weight of PEO.

Despite these numerous studies, there has been no systematic and comprehensive study concerning the blends from hydrophobic PLLA and hydrophilic PVA. In the present study the blends from hydrophobic PLLA and hydrophilic water-insoluble PVA were prepared by solution casting and melt quenching. Their morphology, swelling behavior, and surface and bulk properties were investigated by polarizing optical microscopy, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), X-ray diffractometry, gravimetry, dynamic contact angle measurements, and tensile testing. To exclude the effect of the highly ordered structure of PLLA specimens on their physical properties, solution-cast blends were heated above the melting temperature of

PLLA (ca. 180°C) and then quenched at 0°C because the physical properties of PLLA specimens depend on their highly ordered structure.<sup>8</sup> Heating above the melting temperature of PVA (ca. 230°C) was not performed to avoid thermal degradation of PLLA and transesterification between PLLA and PVA molecules and to leave the PVA microcrystallites acting as crosslinks, which maintained the shape of blend films when immersed in water.

## EXPERIMENTAL

### Materials

PLLA (LACTY®5000,  $M_w = 3.3 \times 10^5$ ,  $M_w/M_n = 1.7$ ) was kindly supplied by Shimadzu Co. and utilized after purification by precipitation using chloroform and methanol as solvent and nonsolvent, respectively, and drying *in vacuo* for 1 week. The PVA (degree of polymerization = 2000, 99.5  $\pm$  0.5% hydrolyzed, atactic) was purchased from Nacalai Tesque Inc. The water-soluble low molecular weight PVA was removed by immersion in distilled water at 37°C for 24 h, followed by drying *in vacuo* for 1 week. Blend films of 100- and 25- $\mu$ m thickness were used for measurements and microscopic observation, respectively, and were prepared by the method described in a previous article.<sup>8</sup> Briefly, the mixed solutions of PLLA and PVA in their different proportions were prepared at a total polymer concentration of 1.0 g/dL using 1,1,1,3,3,3-hexafluoro-2-propanol (Nacalai Tesque Inc., special HPLC grade) as a cosolvent, which was utilized by Pitt et al. for preparation of the blends from P(DLLA-GA) and PVA.<sup>1</sup> These solutions were cast onto a petri dish, followed by solvent evaporation at 25°C for approximately 1 week. The resulting films were dried *in vacuo* for another week and then melted at 200°C for 3 min under a reduced pressure, followed by quenching at 0°C.

### Measurements and Observations

The glass-transition ( $T_g$ ), crystallization ( $T_c$ ), and melting ( $T_m$ ) temperatures and enthalpies of crystallization ( $\Delta H_c$ ) and melting ( $\Delta H_m$ ) of the films (100  $\mu$ m thick) were determined by a Shimadzu DT-50 differential scanning calorimeter. The films (sample weight of ca. 3 mg) were heated at a rate of 10°C/min under a nitrogen gas flow of 50 mL/min. The DSC results were calibrated using

benzophenone, indium, and tin as standards. The crystallinities ( $x_c$ ) of PLLA ( $x_{c,PLLA}$ ) and PVA ( $x_{c,PVA}$ ) in the blend films with different PLLA contents ( $X_{PLLA}$ ) was calculated using the following equations under the assumption that the exothermic peak observed around 100°C was ascribed to the crystallization of PLLA:

$$x_{c,PLLA} (\%) = 100 \cdot (\Delta H_{m,PLLA} + \Delta H_{c,PLLA}) / (X_{PLLA} \cdot 93) \quad (1)$$

$$x_{c,PVA} (\%) = 100 \cdot (\Delta H_{m,PVA}) / [(1 - X_{PLLA}) \cdot 156] \quad (2)$$

$$X_{PLLA} (w/w) = PLLA / (PVA + PLLA) \quad (3)$$

where  $\Delta H_{c,PLLA}$ ,  $\Delta H_{m,PLLA}$ , and  $\Delta H_{m,PVA}$  (J/g of polymer) are the  $\Delta H_c$  of PLLA around 100°C, the  $\Delta H_m$  of PLLA around 170°C, and the  $\Delta H_m$  of PVA around 220°C, respectively; and 93 J/g of PLLA and 156 J/g of PVA are the enthalpies of fusion of the respective PLLA and PVA crystals having infinite crystal thickness.<sup>9,10</sup>

The water absorption ( $A_w$ ) of the films (100  $\mu\text{m}$  thick) immersed in distilled water (Nacalai Tesque, special HPLC grade) at 25°C was evaluated by gravimetry using the following equation:

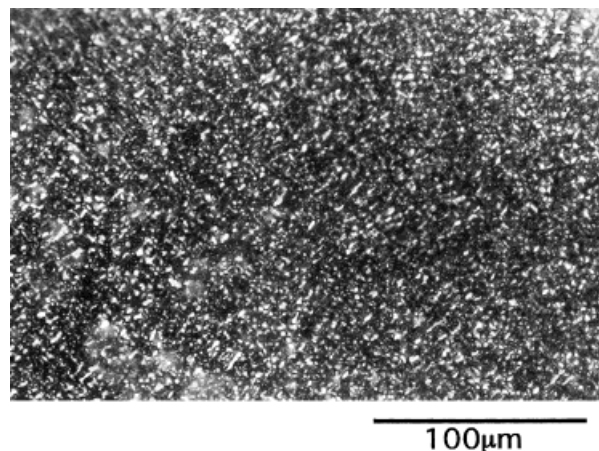
$$A_w (\%) = 100 \cdot (W_a - W_b) / W_b \quad (4)$$

where  $W_b$  and  $W_a$  are the film weights before and after immersion in water, respectively.

The dynamic contact angles (advancing,  $\theta_a$ ; receding,  $\theta_r$ ) of the films were evaluated by a Orientec DCA-100 using the method described by Smith et al.<sup>11</sup> The films were measured at a speed of 20 mm/min in distilled water (Nacalai Tesque, special HPLC grade) at 25°C.

The tensile properties of the 100  $\mu\text{m}$  thick films were measured at 25°C and 50% relative humidity before and after immersion in distilled water for 24 h using a Shimadzu tensile tester (EZ-Test) at a crosshead speed of 20 mm/min. The initial gauge length was always kept at 20 mm.

X-ray diffractometry of the films with a thickness of 100  $\mu\text{m}$  was performed at 25°C using a Rigaku RINT-2500 equipped with a Cu K $\alpha$  source. The morphology of the 25  $\mu\text{m}$  thick films was studied with a Zeiss polarizing microscope and a Hitachi SE microscope (S-2300). The films for SEM observation were coated with carbon to a thickness of about 20 nm.



**Figure 1** A polarizing photomicrograph of the dry blend film with  $X_{PLLA} = 0.5$ .

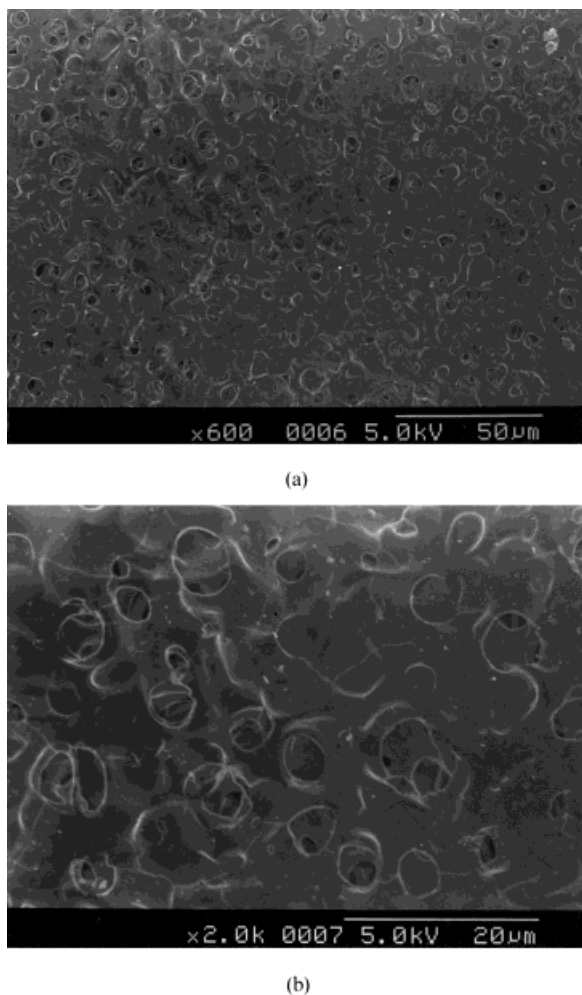
## RESULTS

### Morphology

Figure 1 shows a typical polarizing optical photomicrograph of the melt-quenched blend film with a  $X_{PLLA}$  of 0.5. Numerous spherulites and some relatively dark regions with maximum diameters of about 5  $\mu\text{m}$  were noticed in the blend film and were ascribed to crystallized PVA and amorphous PLLA, respectively. Figure 2 gives SEM photographs of the blend film with a  $X_{PLLA}$  of 0.5 after extraction of PLLA by chloroform and drying *in vacuo*. Pores having an average size of 5  $\mu\text{m}$  were seen in the extracted blend film. This suggested that the PLLA-rich phase formed the domain with a size of 5  $\mu\text{m}$  and the PVA-rich phase was continuous in the blend film before extraction. An extracted weight ratio of the blend film with a  $X_{PLLA}$  of 0.5 by chloroform was 47.5%, which agreed with the expected value. This agreement implied that the PLLA-rich and PVA-rich phases were continuous in the blend film before extraction.

### Thermal Properties

Figure 3 shows DSC thermograms of the melt-quenched films with different  $X_{PLLA}$  values. The  $x_{c,PLLA}$ ,  $x_{c,PVA}$ ,  $T_{m,PLLA}$ ,  $T_{m,PVA}$ ,  $T_{c,PLLA}$ , and  $T_g$  evaluated from Figure 3 are plotted in Figure 4 as a function of  $X_{PLLA}$ . The  $T_{m,PVA}$ ,  $T_{m,PLLA}$ ,  $T_{c,PLLA}$ , and  $T_g$  values of the blend films were approximately constant, irrespective of  $X_{PLLA}$ , although a small decrease of  $x_{c,PVA}$  occurred upon increasing the  $X_{PLLA}$ . The small decrease in  $x_{c,PVA}$  upon in-



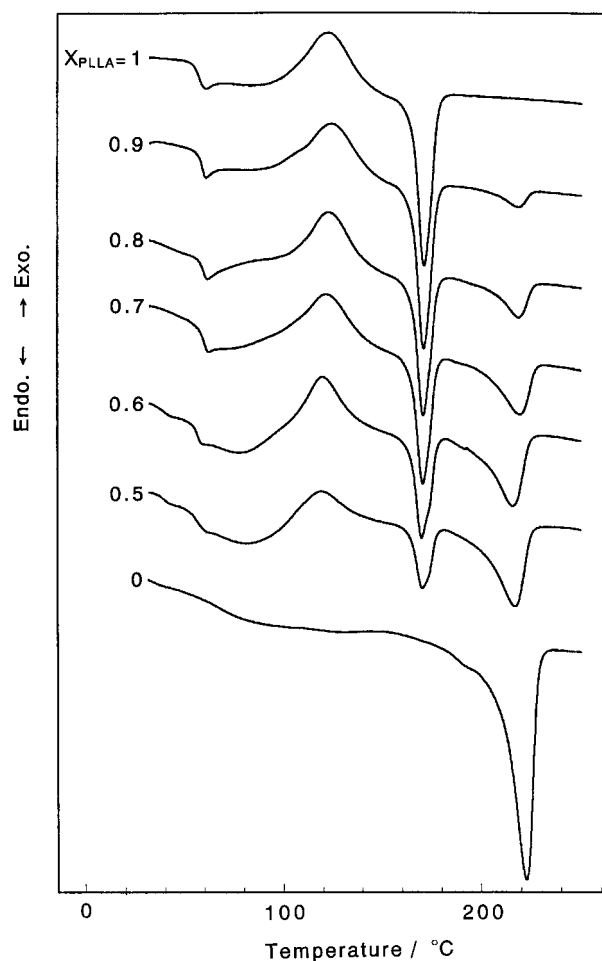
**Figure 2** SEM photographs of (a) the dry blend film with  $X_{\text{PLLA}} = 0.5$  and (b) a magnification of it.

creasing the  $X_{\text{PLLA}}$  implied that PVA was crystallizable but its crystallization was slightly disturbed by the presence of PLLA molecules. A zero  $x_{c,\text{PLLA}}$  value for all the films containing PLLA, regardless of the  $X_{\text{PLLA}}$ , meant that PLLA was amorphous in the blend films and the nonblended PLLA film. The  $x_{c,\text{PVA}}$  values of 32–45% were comparable with those reported for the blends from P(DLLA-GA) and PVA.<sup>1</sup>

In the partially miscible blends from P(DLLA-GA) and PVA the  $T_m$  of PVA was decreased by 20°C by the presence of P(DLLA-GA) and a single  $T_g$  was noticed between the  $T_g$  values of nonblended P(DLLA-GA) and PVA when the P(DLLA-GA) content  $[X_{\text{P(DLLA-GA)}} \text{ (w/w)} = \text{P(DLLA-GA)} / (\text{P(DLLA-GA)} + \text{PVA})]$  was in the range of 0.1–0.3.<sup>1</sup> The decrease in the  $T_m$  of PVA in the blends also suggested that thickening of the PVA crystallites was disturbed by the pres-

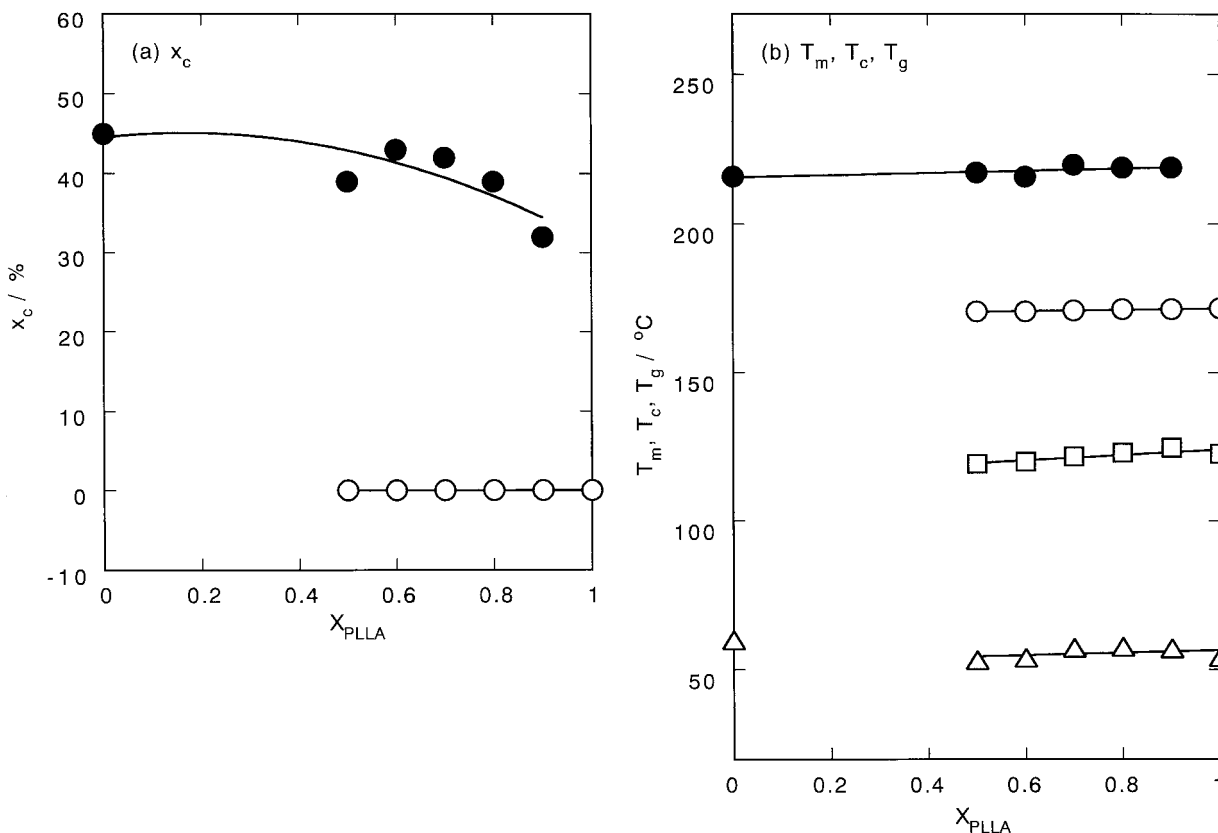
ence of P(DLLA-GA) molecules, resulting in reduced crystalline thickness of PVA in the blends.

The blends from PLLA and PEO were also reported to be partially miscible.<sup>2,3,6,12–14</sup> The  $T_g$  and  $T_c$  values of these blends varied, depending on their blending ratio.<sup>2,3,13,14</sup> The  $T_m$  values of PLLA in the blends were practically constant, regardless of their blending ratio, when the molecular weight of PEO was higher than  $1 \times 10^6$  and the blends were prepared by precipitation from their mixed solutions<sup>2</sup> and their solvent evaporation.<sup>6</sup> On the other hand, the large decrease in the  $T_m$  of PLLA was noticed for the blends with low PLLA contents when the molecular weight of the PEO was as low as  $3 \times 10^3$  and the blends were crystallized during solvent evaporation<sup>12</sup> and under a constant temperature decrease from the melt.<sup>13,14</sup> Park et al. reported a similar decrease in the  $T_m$  of PLLA upon the addition of low molecular weight Pluronic.<sup>4</sup> Two



**Figure 3** DSC thermograms of dry blend films with different  $X_{\text{PLLA}}$  values.





**Figure 4** The (a) crystallinities ( $x_c$ ) and (b) melting ( $T_m$ ), cold crystallization ( $T_c$ ), and glass-transition temperatures ( $T_g$ ) of dry blend films with different  $X_{PLLA}$  values: (○)  $x_{c,PLLA}$ ,  $T_{m,PLLA}$ ; (●)  $x_{c,PVA}$ ,  $T_{m,PVA}$ ; (□)  $T_{c,PLLA}$ ; and (△)  $T_g$ .

studies found the high miscibility of PLLA and PEO at a specific blending ratio, which was evidenced by a very small  $x_c$  value of PLLA in the blend and the appearance of a cold crystallization peak during DSC scanning at this specific ratio.<sup>3,6</sup> The specific ratio depended on the molecular weight of the PEO.<sup>6</sup>

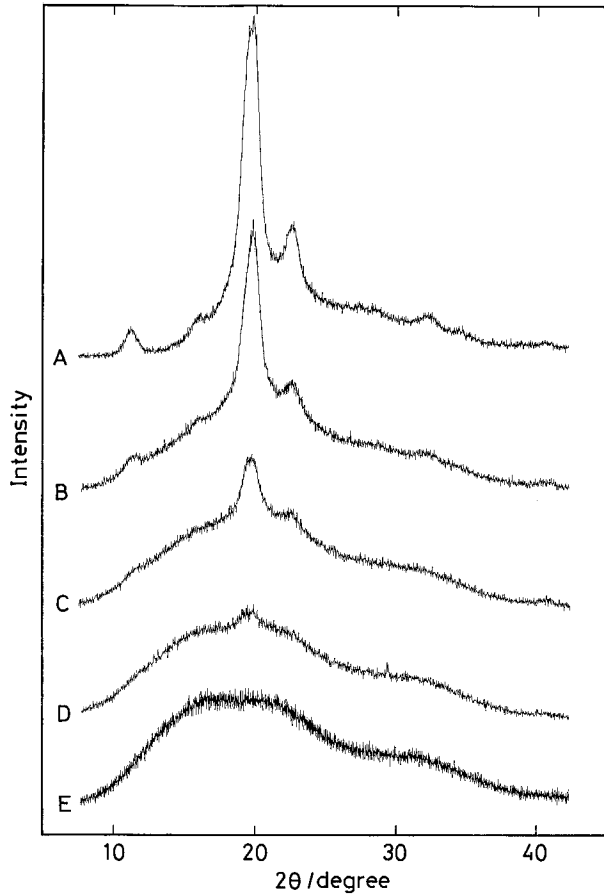
### X-Ray Diffractometry

X-ray diffraction profiles of the blend films are shown in Figure 4. When PLLA crystallized in a pseudo-orthorhombic unit cell (dimensions:  $a = 1.07$  nm,  $b = 0.595$  nm, and  $c = 2.78$  nm), which contained two  $10_3$  helices ( $\alpha$  form), the main peaks in the X-ray diffraction profile appeared at  $2\theta$  values of 15, 17, and 19°. <sup>15-17</sup> However, no such peak appears in Figure 5, meaning that the PLLA in the blend films was completely amorphous, which agreed with the DSC result. On the other hand, the most intense peaks observed at  $2\theta$  values of 19 and 23° for the blend films were ascribed to PVA crystallized in a monoclinic unit

cell (dimensions:  $a = 0.781$  nm,  $b = 0.252$  nm, and  $c = 0.551$  nm,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 91.7^\circ$ ),<sup>18</sup> meaning that PVA was crystallizable in the presence of PLLA in agreement with the results by polarizing optical microscopy and DSC.

### Water Absorption

The  $A_w$  of the blend films with different  $X_{PLLA}$  values is plotted in Figure 6 as a function of immersion time in water. The  $A_w$  increased with immersion time and then reached a plateau in 10 h, regardless of the  $X_{PLLA}$ . Pitt et al. reported that the water content of the blends from P(DLLA-GA) and PVA increased rapidly at an initial stage and then decreased slowly as a result of hydrolysis of P(DLLA-GA).<sup>1</sup> In our case no such slow decrease occurred within the period studied here, probably because of the low hydrolysis rate of PLLA compared with that of P(DLLA-GA). This was evidenced by the hydrolysis rate constant ( $k$ ) values reported for 50/50 P(DLLA-GA) ( $k = 7.44 \times 10^{-2} \text{ day}^{-1}$ )<sup>19</sup> and amorphous PLLA ( $k = 2.59$



**Figure 5** X-ray diffraction profiles of dry blend films with different  $X_{\text{PLLA}}$  values:  $X_{\text{PLLA}}$  = (A) 0, (B) 0.5, (C) 0.7, (D) 0.9, and (E) 1.

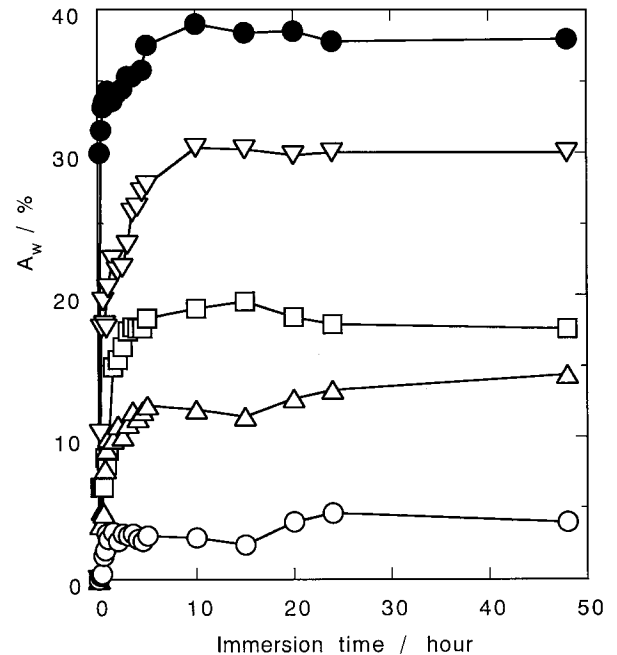
$\times 10^{-3} \text{ day}^{-1}$ ).<sup>20</sup> Figure 7 shows the  $A_w$  of the blend films from PLLA and PVA after immersion in water for 24 h as a function of  $X_{\text{PLLA}}$ , together with that reported by Pitt et al. for the blend films from P(DLLA-GA) and PVA immersed in distilled water for 24 h as a function of  $X_{\text{P(DLLA-GA)}}$ .<sup>1</sup> The water content [ $C_w$  (%)] in the literature<sup>1</sup> was converted to  $A_w$  using the following equation:

$$A_w (\%) = C_w / (1 - C_w / 100) \quad (5)$$

The  $A_w$  of the both blend films decreased monotonously with increasing  $X_{\text{PLLA}}$  and  $X_{\text{P(DLLA-GA)}}$ . The experimental  $A_w$  values of the blends from PLLA and PVA and those from P(DLLA-GA) and PVA were higher and lower, respectively, than expected from the  $A_w$  values of the nonblended films.

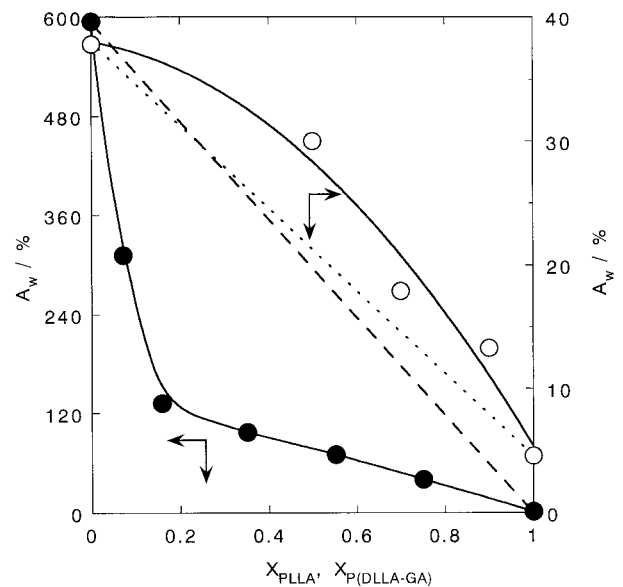
### Contact Angles

The contact angles of the blend films are plotted in Figure 8 as a function of the  $X_{\text{PLLA}}$ . The aver-

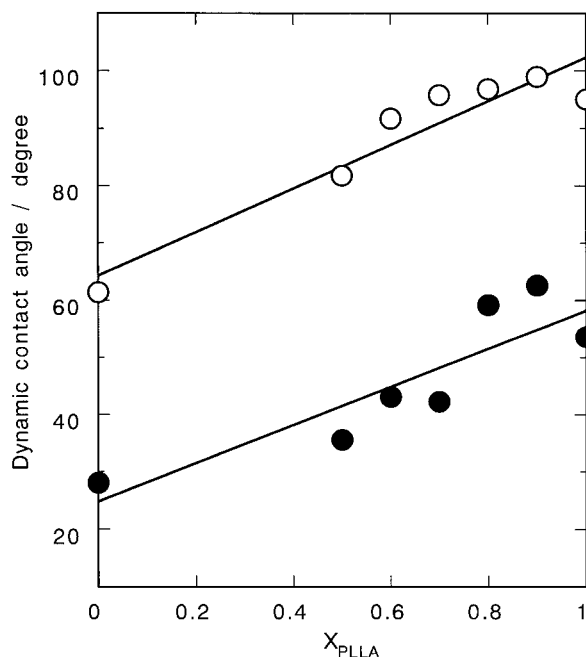


**Figure 6** The water absorption ( $A_w$ ) of blend films with different  $X_{\text{PLLA}}$  values as a function of the immersion time in water:  $X_{\text{PLLA}}$  = (●) 0, (▽) 0.5, (□) 0.7, (△) 0.9, and (○) 1.

age contact angles for nonblended PLLA and PVA were 74 and 45°, respectively; these were comparable with 75 and 42° reported by Tsuchiya et



**Figure 7** The water absorption ( $A_w$ ) of the blend films from (○) PLLA and PVA and those from (●) P(DLLA-GA) and PVA after immersion in water for 24 h as a function of  $X_{\text{PLLA}}$  and  $X_{\text{P(DLLA-GA)}}$ , respectively.



**Figure 8** The (○) advancing ( $\theta_a$ ) and (●) receding ( $\theta_r$ ) contact angles of the blend films as a function of  $X_{\text{PLLA}}$ .

al.<sup>21</sup> and Tamada and Ikada<sup>22</sup> for nonblended PLLA and PVA, respectively, using static methods such as the sessile drop method. Evidently, the  $\theta_a$  and  $\theta_r$  both increased linearly with a rise in the  $X_{\text{PLLA}}$  of the blend films and the contact angles were in good agreement with those expected from nonblended PLLA and PVA films. This strongly suggested the probability that the hydrophilicity of the biodegradable materials based on the PLA family can be controlled by the addition of hydrophilic biodegradable polymers.

### Tensile Properties

The tensile properties of biodegradable polymers in wet and dry states are very important in terms of biomedical, pharmaceutical, and ecological applications in the presence of water. The tensile properties of the dry and wet blend films are plotted in Figure 9 as a function of the  $X_{\text{PLLA}}$ . Note that the tensile strength and Young's modulus of the dry blend films decreased nonlinearly and monotonously with increasing  $X_{\text{PLLA}}$ . A remarkable change of tensile strength and Young's modulus occurred at a  $X_{\text{PLLA}}$  between 0.6 and 0.7. On the other hand, the elongation at break of the dry blend films decreased from 75 to 10% when the  $X_{\text{PLLA}}$  increased from 0 to 0.5, whereas its decrease became smaller when the  $X_{\text{PLLA}}$  increased

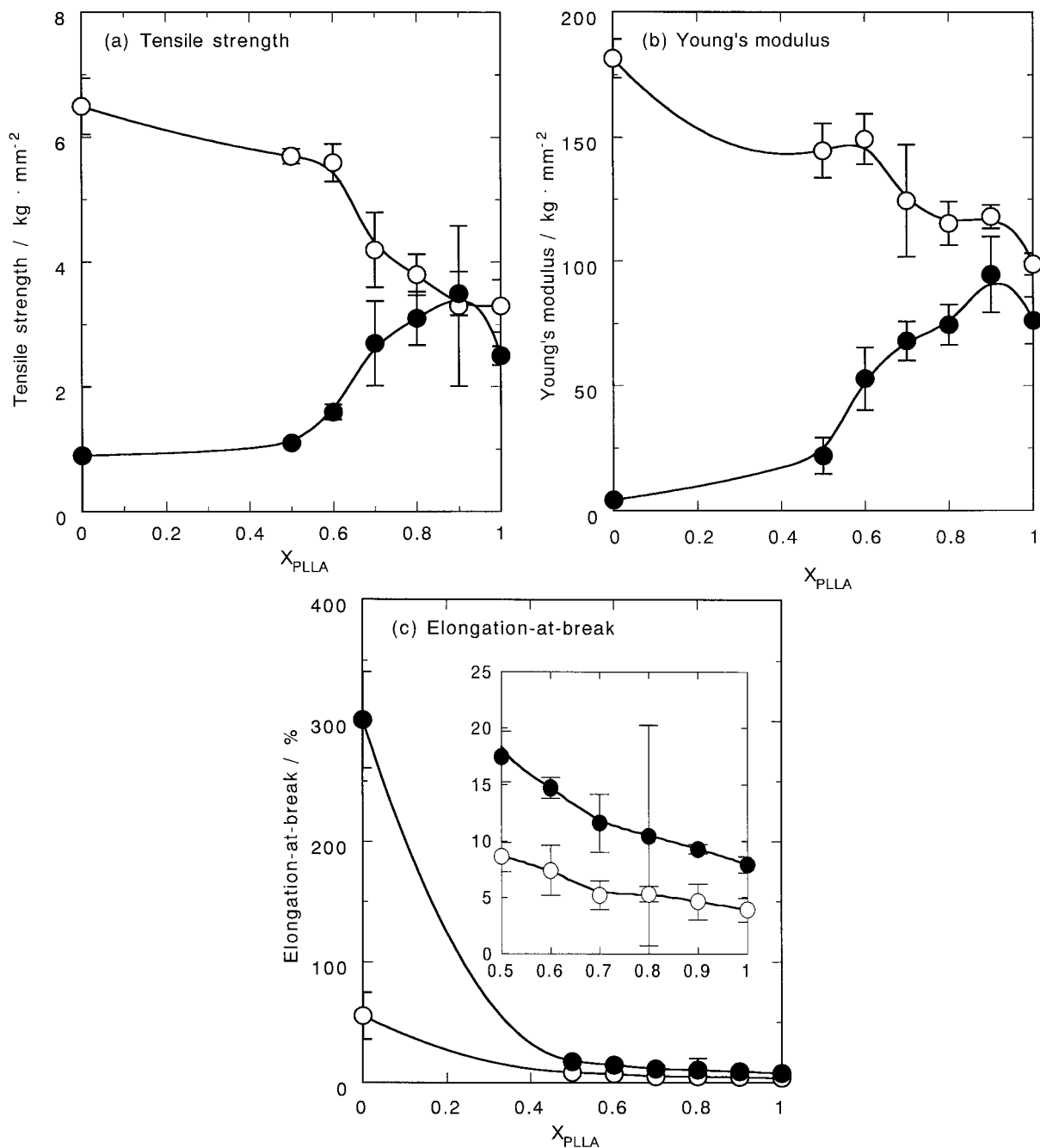
above 0.5. A similar change in tensile properties occurred for the blends from PLLA and water-soluble PEO with an increase in PEO content.<sup>2,3</sup>

The tensile properties of the wet blend films have rather different dependences on the  $X_{\text{PLLA}}$ . Due to large decreases in the tensile strength and Young's modulus of the wet blend films having low  $X_{\text{PLLA}}$  values, their dependence on  $X_{\text{PLLA}}$  was reversed. Namely, they increased with a rise in  $X_{\text{PLLA}}$ . Interestingly, the elongation at break of the wet blend films became higher than that of the dry blend films, irrespective of the  $X_{\text{PLLA}}$  value, and retained the dependence of the elongation at break of dry blend films on the  $X_{\text{PLLA}}$ . These mechanical properties change was because of the swelling of PVA from the presence of water molecules.

### DISCUSSION

We concluded from the results of the polarizing optical microscopy, SEM, DSC, X-ray diffractometry, and tensile testing that PLLA and PVA were phase separated in these blend films after melt quenching. In spite of their phase separation, the slight decreases in  $x_{c,\text{PVA}}$  at high  $X_{\text{PLLA}}$  values (Fig. 4) suggested that a part of the PVA molecules was trapped in an amorphous state in the PLLA-rich phase and/or the PLLA molecules present in the PVA-rich phase reduced the nucleus density of PVA crystallites. Polarizing optical microscopy, SEM, and gravimetry revealed that the PLLA-rich and PVA-rich phases both formed a continuous domain in the blend film with a  $X_{\text{PLLA}}$  of 0.5. The dramatic decrease in tensile strength and Young's modulus of dry blend films at a  $X_{\text{PLLA}}$  higher than 0.6 was ascribed to the morphology change of the PVA-rich phase from continuous to dispersed.

The higher than expected  $A_w$  values of the blend films compared to those of nonblended films (Fig. 7) were probably due to formation of the interfacial area between the PLLA-rich and PVA-rich phases in the blend films, where water molecules were trapped. In contrast, the lower  $A_w$  values of the blend films from P(DLLA-GA) and PVA were attributable to the strong interaction between P(DLLA-GA) and PVA, which may have hindered the interaction between water and PVA or P(DLLA-GA). On the other hand, the experimental values of the contact angles of the blend films from PLLA and PVA agreed well with those expected from nonblended PLLA and PVA films.



**Figure 9** The (a) tensile strength, (b) Young's modulus, and (c) elongation at break of (○) dry and (●) wet blend films as a function of  $X_{\text{PLLA}}$ .

This implied that the surface concentrations of PLLA and PVA were comparable with those of their bulk concentrations. In other words, no enrichment of the constituent polymers occurred at the surfaces of the blend films during solvent evaporation and melt quenching, irrespective of the  $X_{\text{PLLA}}$ . The results of the contact angle measurements also suggested that there was no sig-

nificant interaction between PLLA and PVA. If there was a strong interaction between them, the hydrophilicity of the blend films would decrease due to reduced interaction between water and PVA or PLLA, resulting in increased experimental contact angles of the blend films.

The solubility parameter ( $\delta$ ) values of PLLA, P(DLLA-GA), PVA, and PEO are summarized in



**Table I Solubility Parameter ( $\delta$ ) Values for PLLA, P(DLLA-GA), PVA, and PEO**

Polymer	$\delta$ ( $\text{J}^{0.5} \text{cm}^{-1.5}$ )	Method	Ref.
PLLA	22.7	Calcd (Fedors parameters)	19
	19.0–20.5	Experimental (swelling)	23
P(DLLA-GA) (50/50)	24.4	Calcd (Fedors parameters)	1
	25.1	Calcd (Hoy parameters)	1
PVA	21.6	Calcd	24
	25.8–29.1	Experimental	25, 26
PEO	17.8	Calcd	27
	$20.2 \pm 2$	Experimental (IPGC)	28

The values are from the literature.<sup>1,19,23–28</sup> IPGC, inverse phase gas chromatography.

Table I.<sup>1,19,23–28</sup> The phase separation between PLLA and PVA and the partial miscibility between PLLA and PEO can be expected from the large and small differences, respectively, between the experimental  $\delta$  values of the constituent polymers but not from those between their calculated  $\delta$  values. There is a probability that PLLA and PVA are miscible with each other when the  $X_{\text{PLLA}}$  is lowered below 0.5 as in the blends from P(DLLA-GA)<sup>1</sup> and/or the blends are prepared by different procedures such as melt blending without solvent. Table I cannot explain the miscibility observed for the blend films from P(DLLA-GA) and PVA having a  $X_{\text{P(DLLA-GA)}}$  lower than 0.3. Their high miscibility for a  $X_{\text{P(DLLA-GA)}}$  below 0.3, despite a large difference in their  $\delta$  values, and the deviation of experimental  $A_w$  values of these blend films from those expected from the experimental values of the nonblended P(DLLA-GA) and PVA were explained by the hydrogen bonding between the hydroxyl groups of PVA and the ester groups of P(DLLA-GA).<sup>1</sup> The hydrophilicity and molecular disorder of PLLA must be lower than that of P(DLLA-GA) because of the absence of a relatively hydrophilic glycolide unit in PLLA and the stereoregular sequence of L-lactide units in PLLA compared with the random sequence of L-lactide, D-lactide, and glycolide units in P(DLLA-GA). The high stereoregularity of PLLA promotes intra- and intermolecular interaction as in PLLA crystals. These two factors may have hindered formation of the hydrogen bonding between PLLA and PVA, resulting in their phase separation. The other probable causes for the reduced interaction between PLLA and PVA in this study are as follows: the presence of cosolvent during solvent evaporation, the formation of a PLLA-rich phase by crystallization of PLLA during solvent evapo-

ration, and the formation of a PVA-rich phase by crystallization of PVA during solvent evaporation and/or melt quenching of PLLA. More detailed investigations are required to determine the miscibility between PLLA and PVA. A study of the enzymatic and nonenzymatic hydrolytic behavior of these blend films will be published in the near future.

## CONCLUSION

PLLA and PVA molecules were phase separated in their blend films and PLLA-rich and PVA-rich phases formed a continuous domain in the blend film of with a  $X_{\text{PLLA}}$  of 0.5. The water absorption of the blend films saturated for 10 h and the values at 24 h were higher than expected from the nonblended PLLA and PVA films, which was due to the increased interfacial area between the PLLA-rich and PVA-rich phases. Owing to the swelling of the PVA-rich phase, the dramatic decrease in the tensile strength and Young's modulus and the increase in the elongation at break were recognized in the wet blend films having low  $X_{\text{PLLA}}$  values. The dynamic contact angles of the blend films were linearly increased with an increase in the  $X_{\text{PLLA}}$ , suggesting that no enrichment of the constituent polymers occurred at their surfaces, irrespective of the  $X_{\text{PLLA}}$ . The tensile strength and Young's modulus of the dry blend films decreased with a rise in  $X_{\text{PLLA}}$ , while this inclination was reversed because of their large decrease for the blend films having high  $X_{\text{PLLA}}$  values after immersion in water. The elongation at break was higher for the wet blend film than for the dry blend film when compared at the

same  $X_{\text{PLLA}}$  and that of the dry and wet blend films decreased with an increase in  $X_{\text{PLLA}}$ .

## REFERENCES

- Pitt, C. G.; Cha, Y.; Shah, S. S.; Zhu, K. J. *J Controlled Release* 1992, 19, 189.
- Nijenhuis, A. J.; Colstee, E.; Grijpma, D. W.; Pennings, A. J. *Polymer* 1996, 37, 5849.
- Sheth, M.; Ananda Kumar, R.; Dave, V.; Gross, R. A.; McCarthy, S. P. *J Appl Polym Sci* 1997, 66, 1495.
- Park, T. G.; Cohen, S.; Langer, R. *Macromolecules* 1992, 25, 116.
- Thomson, R. C.; Yaszemski, M. J.; Powers, J. M.; Mikos, A. G. *J Biomater Sci Polym Ed* 1995, 7, 23.
- Tsuji, H.; Smith, R.; Bonfield, W.; Ikada, Y. *J Appl Polym Sci* 2000, 75, 629.
- Tsuji, H.; Ishizaka, T. *J Appl Polym Sci* 2001, 80, 2281.
- Tsuji, H.; Ikada, Y. *Polymer* 1995, 36, 2709.
- Fischer, E. W.; Sterzel, H. J.; Wegner, G. *Kolloid-ZZ Polym* 1973, 251, 980.
- Tubbs, R. K. *Polym Sci Part A* 1965, 3, 4181.
- Smith, L.; Doyle, C.; Gregonis, D. E.; Andrade, J. D. *J Appl Polym Sci* 1982, 26, 1269.
- Younes, H.; Cohn, D. *Eur Polym J* 1988, 24, 765.
- Nakafuku, C.; Sakoda, M. *Polym J* 1993, 25, 909.
- Nakafuku, C. *Polym J* 1996, 28, 568.
- Ikada, Y.; Jamshidi, K.; Tsuji, H.; Hyon, S.-H. *Macromolecules* 1987, 20, 904.
- Sarasua, J.-R.; Prud'homme, R. E.; Wisniewski, M.; Le Borgne, A.; Spassky, N. *Macromolecules* 1998, 31, 3895.
- Kister, G.; Cassanas, G.; Vert, M. *Polymer* 1998, 39, 267.
- Assender, H. Z.; Windle, A. H. *Polymer* 1998, 39, 4295.
- Cha, Y.; Pitt, C. G. *Biomaterials* 1990, 11, 108.
- Tsuji, H.; Mizuno, A.; Ikada, Y. *J Appl Polym Sci*, to appear.
- Tsuchiya, F.; Tomida, Y.; Fujimoto, K.; Kawaguchi, H. *Polym Prepr Jpn* 1993, 42, 4916.
- Tamada, Y.; Ikada, Y. *J Colloid Interface Sci* 1993, 155, 334.
- Tsuji, H.; Sumida, K. *J Appl Polym Sci* 2001, 79, 1587.
- Coleman, M. M.; Serman, C. J.; Bhagwagar, D. E.; Painter, P. C. *Polymer* 1990, 31, 1187.
- Van Krevelen, D. W., Ed. *Properties of Polymers. Their Estimation and Correlation with Chemical Structure*; Elsevier: Amsterdam, 1976; p 136.
- Ciemniecki, S. C.; Glasser, W. G. *Polymer* 1988, 29, 1030.
- Mieczkowski, R. *Eur Polym J* 1991, 27, 377.
- Dipaola-Baranayi, G. *Macromolecules* 1982, 15, 622.