

# Thermally Induced Phase Separation in Poly(lactic acid)/Dialkyl Phthalate Systems

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**Abstract:** Thermally induced phase separation in poly(lactic acid)/dialkyl phthalate systems was investigated. Poly(DL-lactic acid) (PDLLA) and poly(L-lactic acid) (PLLA) with different molecular weights were used. A series of dialkyl phthalates, with different numbers of carbon atoms in the alkyl chain, were employed as solvents to control the interaction between polymer and solvent. The liquid–liquid phase-separation temperature of the poly(lactic acid) solutions decreased systematically with a shorter alkyl chain in the phthalate. Based on the interaction between polymer and solvent and the molecular weight of polymer influencing

liquid–liquid phase-separation temperature significantly but crystallization temperature only slightly, proper thermal conditions were employed to investigate competitive phase separation and crystallization in PLLA solutions. Factors that can influence the final morphology of PLLA solutions were examined. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2224–2232, 2003

**Key words:** poly(lactic acid); thermally induced phase separation; phase diagram; morphology

## INTRODUCTION

Thermally induced phase separation (TIPS) is a versatile and simple technique for the preparation of microporous membranes.<sup>1–9</sup> Since its development in the early 1980s,<sup>10</sup> much attention has been focused on its applicability to insoluble polymers at room temperature and its utility for morphology control with fewer variables. The TIPS process is based on the phenomenon that solvent effectiveness decreases when temperature is decreased. When a homogeneous solution at elevated temperature is cooled down, phase separation occurs, resulting in the formation of a polymer-rich phase and a polymer-lean phase. After the solvent is removed, a microporous structure can be obtained.

During the TIPS process the phase transitions may proceed in combinations of liquid–liquid phase separation and solidification such as vitrification,<sup>11</sup> crystallization of the polymer,<sup>12,13</sup> or freezing of the solvent.<sup>14</sup> In most cases these solidifications are useful for

fixing the structure of the solution at a certain stage during liquid–liquid phase separation. The final morphology of the solution is determined by the extent of the liquid–liquid phase separation before solidification. Therefore, the structure of the membrane depends on the competing phase transition between the liquid–liquid phase-separation and solidification processes, and it can be controlled when the relationship between liquid–liquid phase separation and other phase transitions is understood.

In this study we were concerned with TIPS in poly(lactic acid) solutions. Both poly(L-lactic acid) (PLLA) and poly(DL-lactic acid) (PDLLA) with different molecular weights were used to investigate the effects of crystallization of polymer in the same solvent system. Poly(lactic acid) is a promising material for tissue engineering,<sup>15,16</sup> and fabrication of a scaffold via the TIPS process has been reported.<sup>17–19</sup> A series of dialkyl phthalates were adopted as solvents. The interaction between polymer and solvent was systematically controlled by changing the number of carbon atoms in the alkyl chain of the phthalates. Because poly(lactic acid) is relatively polar,<sup>20</sup> it was expected that the solvent power would decrease with an increasing length of the alkyl chain in the phthalate. In this study the relationship between liquid–liquid phase separation

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**TABLE I**  
**Number Average Molecular Weight ( $M_n$ ), Weight-Average Molecular Weight ( $M_w$ ), and Polydispersity ( $M_w/M_n$ ) of Polymers**

	$M_n$	$M_w$	Polydispersity
PLLA	46,000	83,000	1.79
	67,000	138,000	2.06
	168,000	397,000	2.36
PDLLA	10,000	12,000	1.23
	44,000	94,000	2.12
	118,000	226,000	1.92

and crystallization and its effect on the final morphology were investigated.

## EXPERIMENTAL

### Materials

Semicrystalline PLLA and amorphous PDLLA were synthesized or purchased from Polysciences, Inc. (Warrington, PA). Three kinds of PLLA and PDLLA with different molecular weights were used. Their molecular weights, obtained from GPC, are listed in Table I. The solvents used were 1,2-dialkyl phthalates with different numbers of carbon atoms in the alkyl chain. Solvation quality can be controlled by changing the quantity of these alkyl-chain atoms. The molecular characteristics of the solvents, which were used as received, are summarized in Table II. The effects of polydispersity of the polymer were not considered in this study.

### Optical microscopy

Liquid-liquid phase-separation temperatures were observed with an optical microscope (Leica DMLB, Wetzlar, Germany). Thermal treatments were done on a hot stage (Mettler FP82, Greifensee, Switzerland) and controller (Mettler FP80H, Greifensee, Switzerland). Poly(lactic acid) was dissolved in chloroform to obtain about a 1 wt % solution, which was poured on aluminum dishes and dried at room temperature. Poly(lactic acid) films were obtained and rinsed with methanol and then dried in a vacuum oven at 50°C in order to remove residual solvents. The thickness of the prepared films was 1–3  $\mu\text{m}$ . The polymer films were weighed and placed on a concave microslide, on

which 1,2-dialkyl phthalate was introduced in order to obtain a given concentration. Then a cover glass was placed over the specimen for optical microscopy. The samples were slowly heated to 10°C above the liquid-liquid phase-separation temperature. If the melting point was higher than the liquid-liquid phase-separation temperature, the sample was heated to 10°C above the melting point. Heating was continued for 5 min to ensure homogeneous solution. The cooling and heating rates for observation of the phase-transition temperature were 10°C/min. The temperatures during the experiment ranged from 30°C to 175°C. In this experimental temperature range evaporation of the solvent was negligible.

### Differential scanning calorimetry

Thermal analysis was carried out in a nitrogen atmosphere using a Du Pont DSC model 2010 to observe the crystallization temperature. The temperature was increased from 25°C to 190°C, at which it was kept for 5 min, and then cooled to -20°C. To measure the crystallization temperature, the temperature was increased again from -20°C to 190°C, kept for 5 min at that temperature, and then cooled. All DSC runs were carried out at a scanning rate of 10°C/min.

### Scanning electron microscopy

Poly(lactic acid) and alkyl phthalate were weighed in a stainless-steel mold and dissolved at 200°C for 1 h in a nitrogen atmosphere. Evaporation of the solvent was negligible. The dissolved polymer solutions were quickly moved to a predetermined low temperature in order to obtain phase separations and kept at that temperature for 24 h. Then the samples were immersed in hexane for 48 h at room temperature to extract the solvent. The solvent-free samples were dried in a vacuum oven for more than 2 days. Finally, the samples were fractured in liquid nitrogen to observe the morphology of the sample cross sections, which were examined using a Philips 535M scanning electron microscope (SEM) after receiving a 20- to 25-nm-thick gold coating.

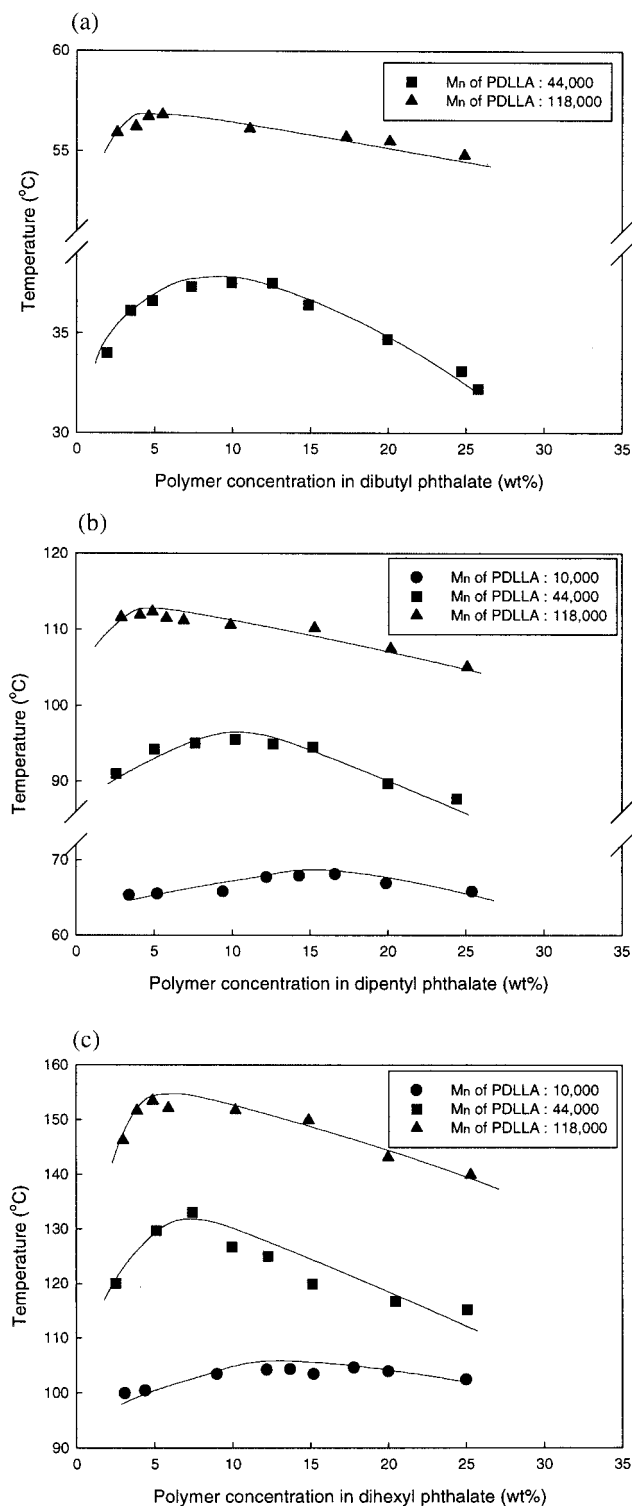
## RESULTS AND DISCUSSION

### Experimental phase diagrams of PDLLA solutions

Experimental phase diagrams of the PDLLA solutions are shown in Figures 1 and 2. Only liquid-liquid

**TABLE II**  
**Molecular Weight, Density, Boiling Point, and Supplier of Solvents**

Solvent	MW	Density at 25°C (g/cm <sup>3</sup> )	Boiling point (°C)	Supplier
Dibutyl phthalate	278.35	1.043	340/760 mm Hg	Aldrich
Dipentyl phthalate	306.39	1.025	342/760 mm Hg	TCI
Dihexyl phthalate	334.45	1.008	210/5 mm Hg	PFALTZ & BAUER



**Figure 1** Liquid-liquid phase-separation temperature determined by optical microscopy for PDLLA solutions in (a) dibutyl phthalate, (b) dipentyl phthalate, and (c) dihexyl phthalate.

phase separation was observed for the amorphous PDLLA solutions. Liquid-liquid phase-separation temperatures were determined by optical microscopy with a scanning rate of 10°C. The observed transitions

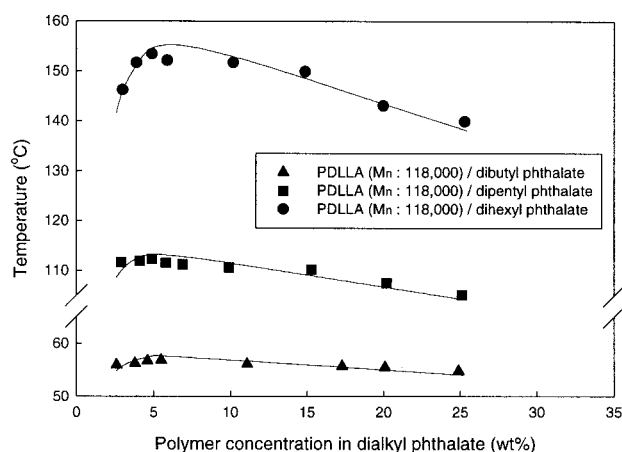
were not equilibrium transitions as nonequilibrium phenomena should be involved. Three kinds of dialkyl phthalate, from butyl to hexyl, were used as solvents for the characterization of the liquid-liquid phase separation. With the PDLLA/dibutyl phthalate system, when a low-molecular-weight polymer ( $M_n$  of 10,000) was used, liquid-liquid phase separation was not observed in the experimental temperature range because it should occur below room temperature. The compositions in which liquid-liquid phase separation temperatures were highest are shown in Figures 1 and 2; these compositions were in good agreement with the critical compositions calculated from the Flory-Huggins theory, as shown in Table III,<sup>21</sup> for which the composition was converted into a weight percentage:

$$\phi_c^{vol} = \frac{1}{1 + \sqrt{r}} \quad (1)$$

$$\phi_c^{wt} = \frac{\phi_c^{vol} \left( \frac{\rho_{polymer}}{\rho_{solvent}} \right)}{1 + \phi_c^{vol} \left( \frac{\rho_{polymer}}{\rho_{solvent}} - 1 \right)} \quad (2)$$

where  $\phi_c^{vol}$  and  $\phi_c^{wt}$  represent the critical composition in the volume and weight fractions, respectively, of polymer;  $r$  denotes the molar volume ratio of polymer to solvent, and  $\rho$  is the density [the density of poly(lactic acid) is available from the literature<sup>22</sup>].

The effect of molecular weight on the phase diagram is shown in Figure 1. As the molecular weight of polymer is increased, the critical composition is shifted to the lower concentration of polymer. The liquid-liquid phase-separation temperature of PDLLA solutions increased with increasing molecular weight of the polymer. Figure 2 shows the effect of solvent on the liquid-liquid phase-transition temperature for the



**Figure 2** Liquid-liquid phase-separation temperature determined by optical microscopy for PDLLA solutions in dialkyl phthalate.

TABLE III  
Critical Concentration of Polymer in Weight Percent Calculated Based on Flory–Huggins Theory

Solvent	$M_n$ of PLLA			$M_n$ of PDLLA		
	46,000	67,000	168,000	10,000	44,000	118,000
Dibutyl phthalate	9.24	7.78	5.06	17.92	9.39	5.98
Dipentyl phthalate	9.73	8.20	5.34	18.77	10.03	6.30
Diethyl phthalate	10.20	8.60	5.61	19.58	10.68	6.62

pair of PDLLA ( $M_n$  of 118,000) and dialkyl phthalate. When the solvent was changed from dibutyl phthalate to diethyl phthalate, the highest liquid–liquid phase-separation temperature increased from 58°C to 154°C. Thus, as the number of the carbon atoms in dialkyl phthalate was increased, liquid–liquid phase separation occurred in a higher temperature region.

### Experimental phase diagram of PLLA solutions

When a crystallizable polymer is used in the TIPS process, there is a possibility that liquid–liquid phase

separation will be coupled with crystallization.<sup>12,13,23–25</sup> We observed liquid–liquid phase separation and crystallization in PLLA solutions on cooling. Liquid–liquid phase-separation temperatures were observed by optical microscopy, and crystallization temperatures were measured by DSC. The phase-transition temperatures were observed at a cooling rate of 10°C/min. Experimental phase diagrams of PLLA with three different molecular weights were constructed. A series of dialkyl (butyl to hexyl) phthalates were employed as solvents. In the PLLA/dibutyl phthalate system, the liquid–liquid phase-separation temperature could not be observed because crystallization occurred prior to liquid demixing during cooling. This will be discussed in detail later.

The effects of PLLA of a particular molecular weight in a given solvent system are shown in Figure 3. As the molecular weight of PLLA increased, the liquid–liquid phase-separation temperature increased, but crystallization temperature remained almost constant. The trend for critical temperature and composition varied in a manner similar to that observed in the PDLLA solutions. The effect of phthalate solvent on the PLLA ( $M_n$  of 67,000) is shown in Figure 4. The liquid–liquid phase-separation temperature decreased significantly, whereas the crystallization temperature was nearly constant with a better solvent (shorter alkyl chain in the phthalate). When either diethyl phthalate or di-

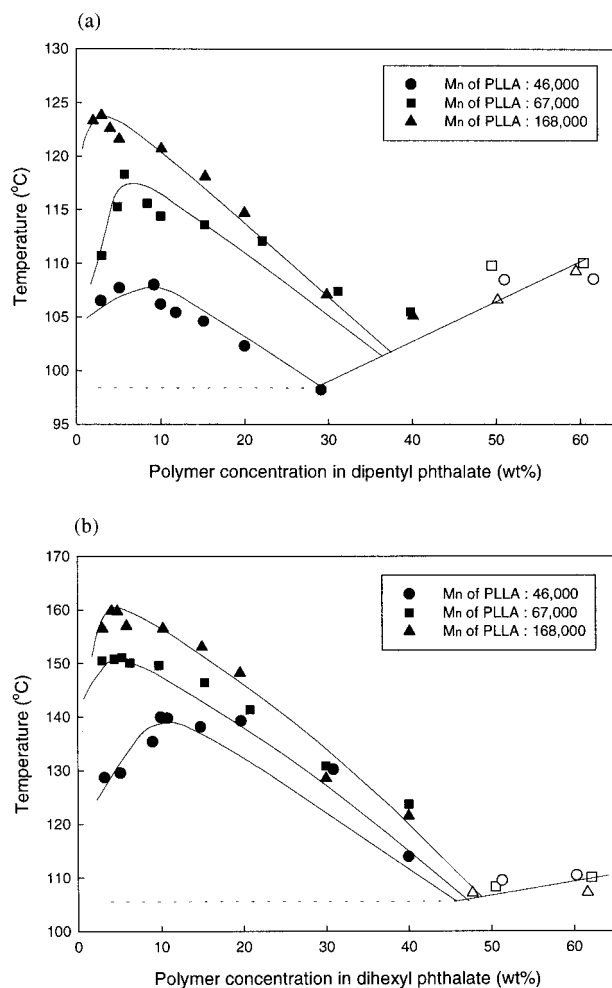


Figure 3 Liquid–liquid phase-separation temperature determined by optical microscopy (filled symbols) and crystallization temperature by DSC (open symbols) for PLLA solutions in (a) dipentyl phthalate and (b) diethyl phthalate.

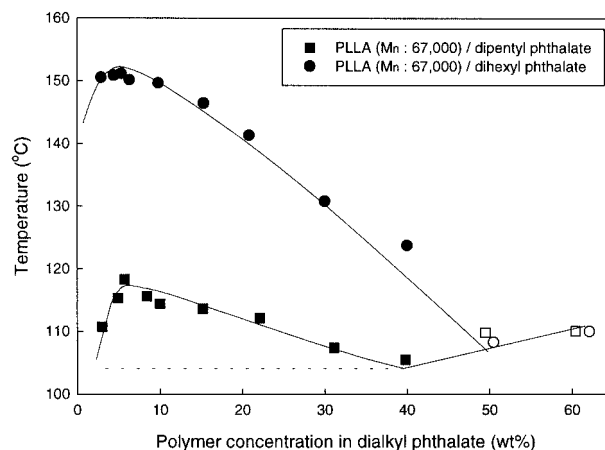
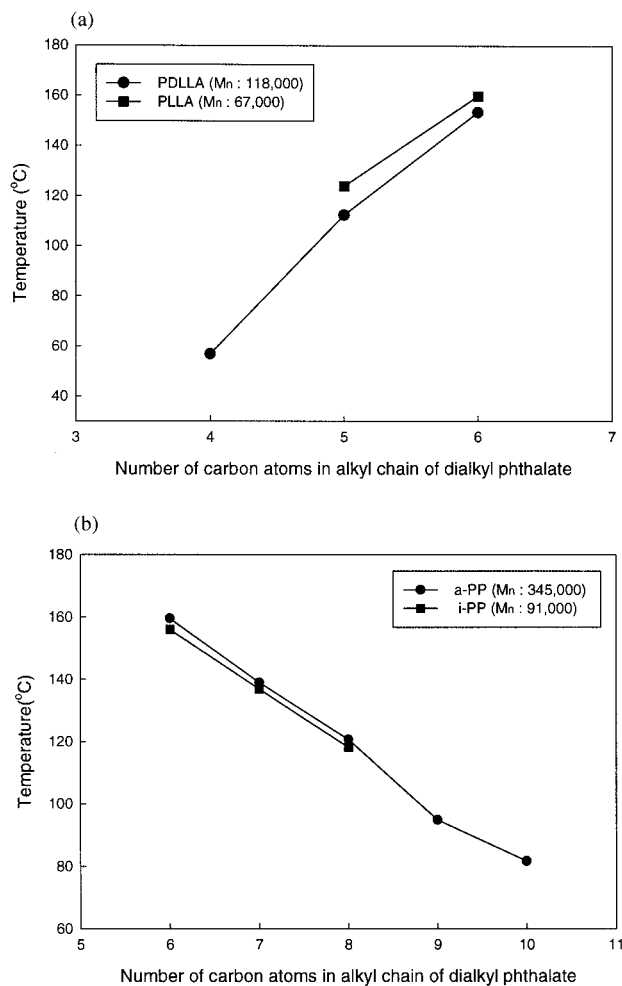


Figure 4 Liquid–liquid phase-separation temperature determined by optical microscopy (filled symbols) and crystallization temperature by DSC (open symbols) for PLLA solutions in dialkyl phthalate.

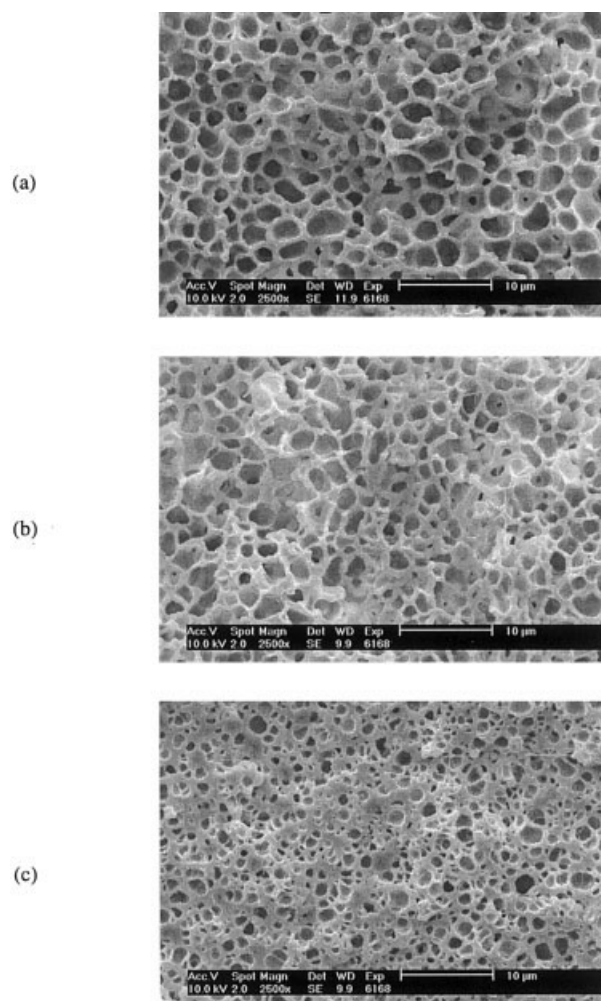


**Figure 5** UCST (highest liquid-liquid phase-separation temperature) for polymer solution in dialkyl phthalate of (a) poly(lactic acid) and (b) polypropylene.<sup>13</sup>

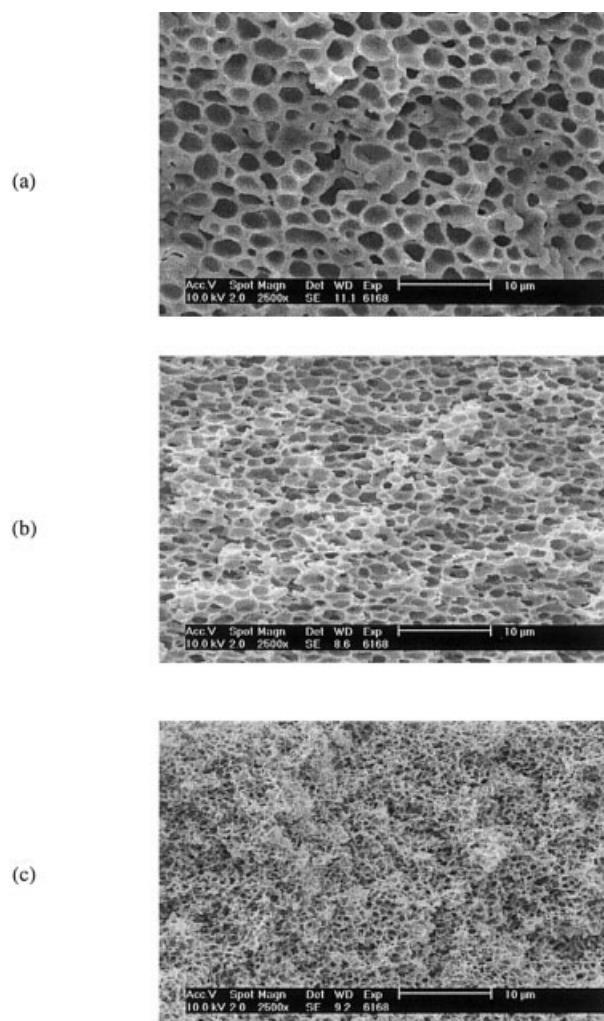
pentyl phthalate was used as a solvent, liquid-liquid phase separation occurred before crystallization at a low concentration of PLLA. With dibutyl phthalate, however, liquid-liquid phase separation was not observed before crystallization in the whole composition because it would occur below the crystallization temperature. This point can be clearly understood when the effect of the solvent quality on liquid demixing and crystallization is considered. Figure 5(a) shows the highest liquid-liquid phase-separation temperature for poly(lactic acid) solutions in dialkyl phthalate. When diheptyl phthalate was used as a solvent, we were not able to observe liquid demixing properly because of evaporation of the solvent on the cover glass and degradation of the polymer. On the other hand, when dibutyl phthalate was used, the crystallization temperature of the PLLA solution remained about 110°C, but liquid-liquid phase separation occurred near 70°C, as was expected [Fig. 5(a)]. Thus, it is possible to use PDLLA to probe the liquid-liquid phase-separation temperature of PLLA solution that

exists below its crystallization temperature with the same solvent system because PDLLA is not crystallizable. Similar reasoning applies for polypropylene solutions. Atactic polypropylene (a-PP) can be used instead of isotactic polypropylene (i-PP) in order to investigate liquid demixing of i-PP solutions with the same solvent as that suggested by Figure 5(b).

Lee et al. investigated liquid-liquid phase separation and crystallization of the i-PP solutions with a series of dialkyl phthalates.<sup>13</sup> It was reported that, as the number of carbon atoms in the dialkyl phthalate decreased, the liquid-liquid phase-separation temperature increased, and the crystallization temperature remained almost constant. The dependence of the liquid-liquid phase-separation temperature on the length of the alkyl chain in the phthalate in polypropylene solutions, interestingly, was contrary to the results observed in the poly(lactic acid) solutions in the same solvent system, as shown in Figure 5. This difference was a result of the hydrophobicity of the polymer. Because polypropylene is considerably more



**Figure 6** SEM micrographs of cross section for 10 wt % PLLA in dipentyl phthalate quenched to 10°C; the  $M_n$  values of PLLA are (a) 46,000, (b) 67,000, and (c) 168,000.



**Figure 7** SEM micrographs of cross section for 10 wt % PLLA in dihexyl phthalate quenched to 10°C; the  $M_n$  values of PLLA are (a) 46,000, (b) 67,000, and (c) 168,000.

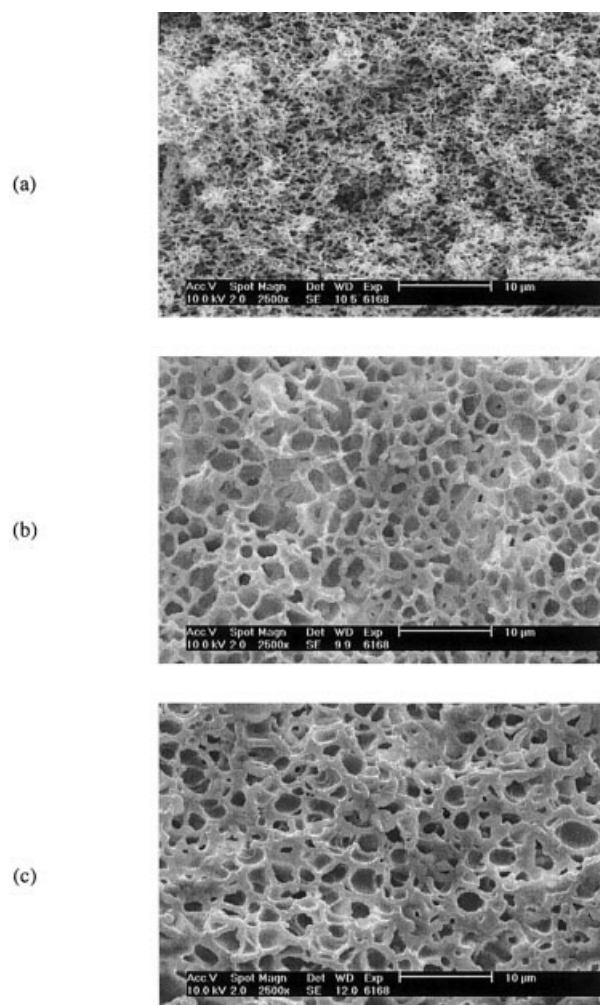
hydrophobic than poly(lactic acid), liquid–liquid phase-separation temperature of polypropylene solutions decreased with an increase in hydrophobic solvents (longer alkyl chain in the phthalate).

### Morphology

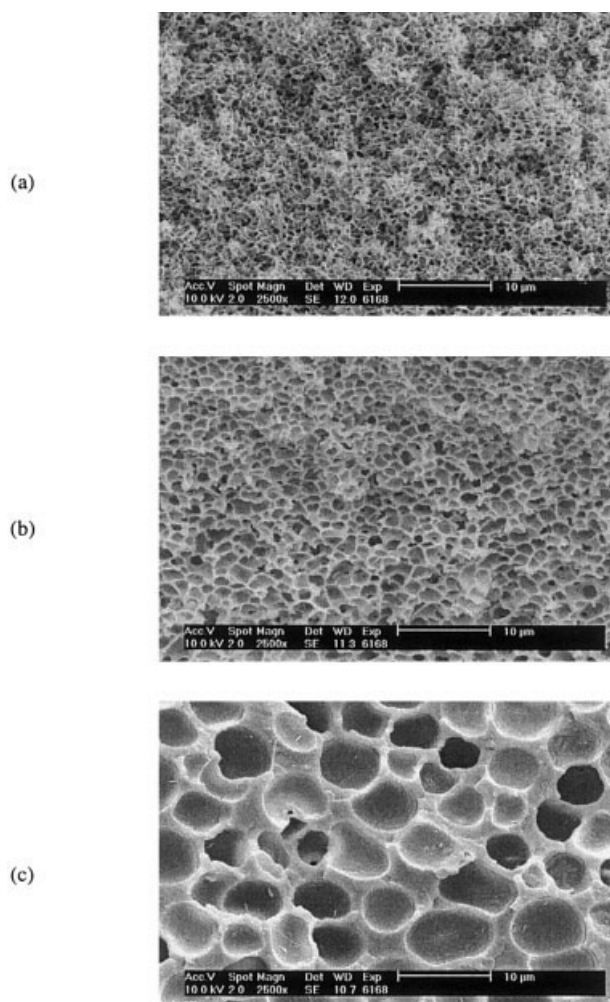
For this study we investigated various factors that could influence the final morphology obtained in PLLA solutions. The porous structure of PDLLA solutions could not be effectively observed because the formed morphology collapsed during evaporation of hexane; thus, it will not be discussed in this article. When a homogeneous semicrystalline polymer solution is cooled, morphology is determined by the competing kinetics of liquid–liquid phase separation and crystallization. The crystallization process can fix the structure obtained by liquid–liquid phase separation. The driving force (quench depth) for both liquid–liquid phase separation and crystallization can be al-

tered systematically because the binodal curve is strongly influenced by the solvent quality, but the crystallization temperature stays nearly constant.<sup>13,23</sup>

The effect of molecular weight on morphology in this study is shown in Figures 6 and 7. At a given polymer concentration and at the same quenching temperature, the pore size of the dried sample decreased with an increasing molecular weight of polymer. This trend can be attributed to the difference in viscosity of the solutions, which slowed down the phase-separation rate. Pore size was determined by the extent of phase separation before crystallization of the polymer-rich phase. As the molecular weight of the polymer was increased for a given concentration of polymer, the viscosity of the solution became high, and the mobility of the molecules was decreased. Therefore, progress of the liquid–liquid phase separation was retarded. Liquid–liquid phase separation progressed more rapidly with a low-molecular-weight polymer than with one with a high molecular weight.



**Figure 8** SEM micrographs of cross section for 10 wt % PLLA ( $M_n$  of 67,000) in a solvent quenched to 10°C; the solvents are (a) dibutyl phthalate, (b) dipentyl phthalate, and (c) dihexyl phthalate.

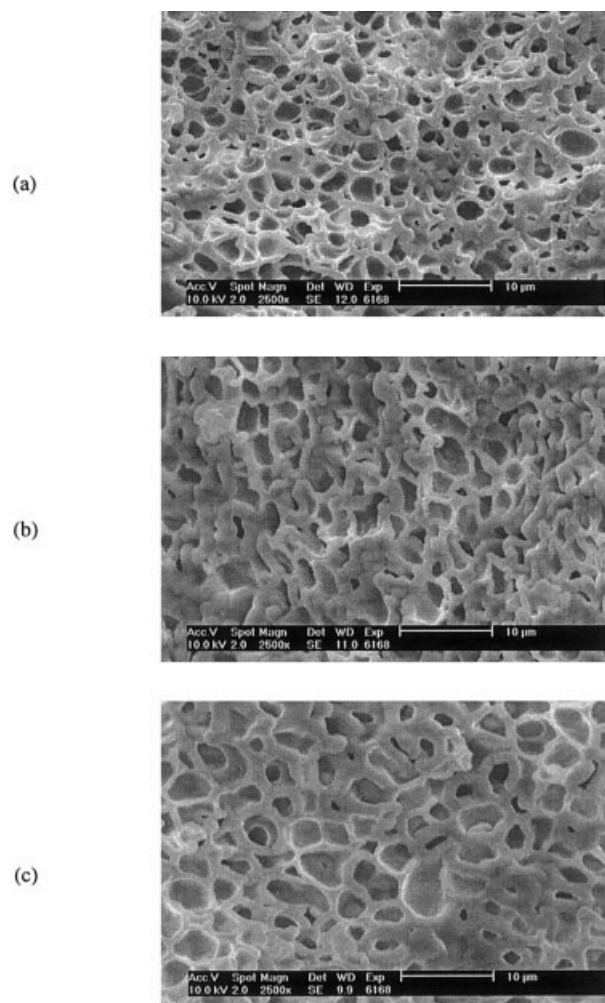


**Figure 9** SEM micrographs of cross section for 10 wt % PLLA ( $M_n$  of 46,000) in a solvent quenched to 30°C; the solvents are (a) dibutyl phthalate, (b) dipentyl phthalate, and (c) dihexyl phthalate.

Figures 8 and 9 show the effects of solvent on the morphology. If the temperature quickly dropped below the crystallization temperature, crystallization could freeze the evolution of liquid–liquid phase separation. The quenching temperatures in this system (10°C and 30°C) were low enough for crystallization of the polymer-rich phase. At a given polymer concentration and at the same quenching temperature, the liquid–liquid phase-separation temperature was changed more significantly than was the crystallization temperature with a change of solvent. As the interaction between polymer and solvent strengthened, the liquid–liquid phase-separation temperature decreased significantly, whereas the crystallization temperature was kept nearly constant. For this reason, the driving force for liquid–liquid phase separation became small in a more powerful solvent. As solvent power increases, the extent of liquid–liquid phase separation should decrease. Because coarsening occurs to reduce the interfacial energy in the later stage of liq-

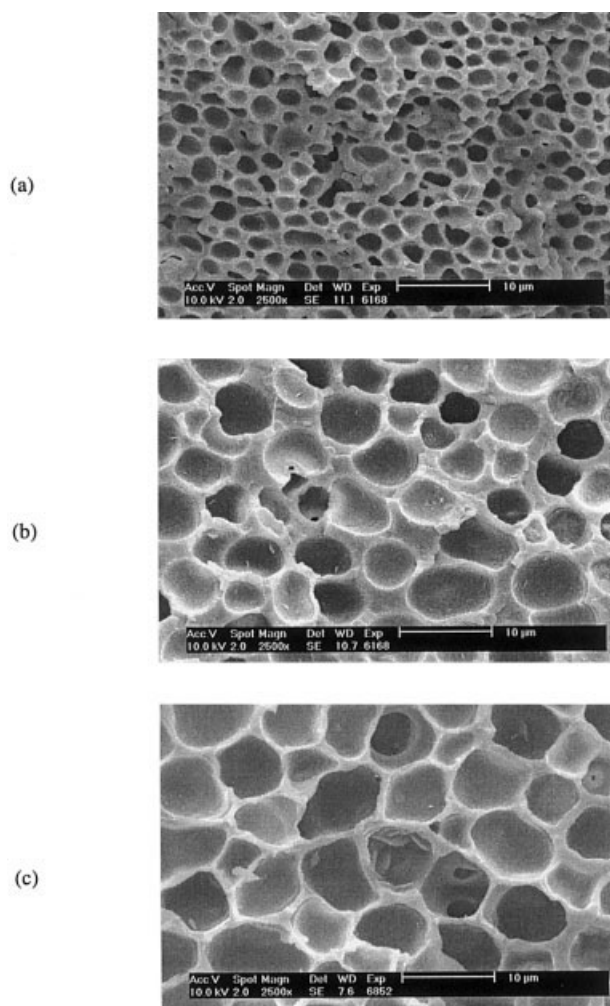
uid–liquid phase separation,<sup>5,26–28</sup> the pores (the polymer-lean phase) formed in a solvent of low power become large. It is interesting to note that the porous structure resulting from liquid–liquid phase separation in PLLA solutions in dibutyl phthalate is evident in Figures 8(a) and 9(a), although we were not able to observe liquid–liquid phase separation at a cooling rate of 10°C/min prior to crystallization by optical microscopy. This could be attributed to the liquid–liquid phase separation preceding crystallization on rapid quenching because of the high nucleation barrier of the crystallization of polymer.<sup>12,23</sup>

In a semicrystalline polymer solution the competing kinetics of liquid–liquid phase separation and crystallization can occur under proper conditions. In our experiment all the quenching temperatures were set below the crystallization temperatures of PLLA solutions, and so the morphology should have been dictated by the two competing kinetic processes. To investigate this phenomenon systematically, the thermal



**Figure 10** SEM micrographs of a cross section of 10 wt % PLLA ( $M_n$  of 67,000) in dihexyl phthalate; the quenching temperatures are (a) 10°C, (b) 30°C, and (c) 50°C.





**Figure 11** SEM micrographs of a cross section of 10 wt % PLLA ( $M_n$  of 46,000) in dihexyl phthalate; the quenching temperatures are (a) 10°C, (b) 30°C, and (c) 50°C.

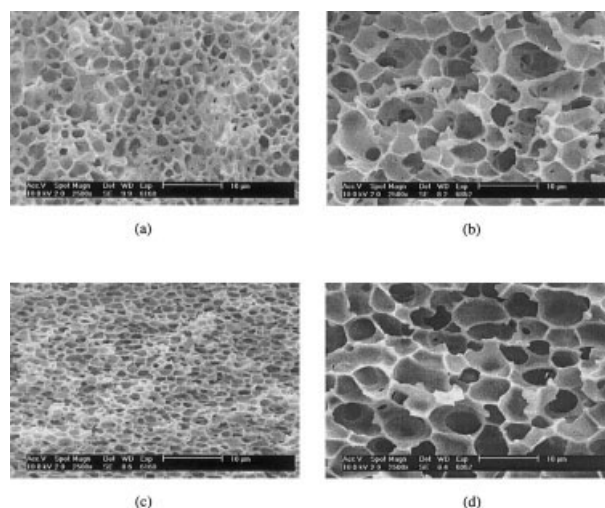
conditions were controlled. As the quenching temperature was decreased, the driving forces for liquid–liquid phase separation and for crystallization were increased. Because crystallization is much more sensitive to temperature than liquid–liquid phase separation, crystallization should play a significant role in morphology formation with decreasing quenching temperature. The morphology changes with quenching temperature in this study are shown in Figures 10 and 11. The liquid–liquid phase separation was dominant at a high quenching temperature because the crystallization rate was relatively slow. Moreover, the mobility of the polymer chain was greater at a higher quenching temperature. Thus, the pore size became large when the quenching temperature was 50°C. When the solution is quenched to a low temperature, 10°C, the crystallization may lock-in the structure obtained by liquid–liquid phase separation at an earlier stage because of rapid crystallization. For this reason, the pore size decreased when the quenching temperature was low, as shown in Figures 10(a) and 11(a).

The viscosity of the solution influences the phase-separation behavior in polymer solutions. The morphologies obtained from solutions of different polymer concentration are shown in Figure 12. The pore size remained almost the same regardless of the quenching temperature in a given concentration of polymer. These results suggest that the effect of PLLA concentration is more significant than that of the quenching temperature under the applied thermal conditions, indicating that the rate of liquid–liquid phase separation is increased by decreasing the polymer concentration because of the low viscosity of the medium and the ease of diffusion of polymer chains. A comparison of the pore sizes obtained from the 3 wt % and 10 wt % solutions clearly indicates the medium's viscosity effect on the rate of phase separation.

## CONCLUSIONS

Experimental phase diagrams for poly(lactic acid)/dialkyl phthalate systems were constructed. When the molecular weight of PLLA was increased, the liquid–liquid phase separation occurred at a higher temperature, and the crystallization temperature remained almost constant. As the number of carbon atoms of the alkyl chain in the phthalate was decreased, liquid–liquid phase-separation temperature decreased considerably, whereas the crystallization temperature was not significantly influenced.

The final morphology of the PLLA solutions was investigated by changing the variables of the TIPS process. The pore size increased when the quenching temperature and the solvent quality were decreased, which allowed liquid–liquid phase separation to



**Figure 12** SEM micrographs of a cross section for PLLA ( $M_n$  of 67,000) solutions in dipentyl phthalate; polymer concentrations and quenching temperatures are: (a) 10 wt % and 10°C; (b) 3 wt % and 10°C; (c) 10 wt % and 30°C; and (d) 3 wt % and 30°C.



progress further before crystallization. When the polymer concentration was low and the PLLA molecular weight was decreased, the rate of liquid–liquid phase separation increased because of low viscosity and ease of diffusion, so large pores were obtained.

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