

Crystallization Behavior of Poly(ϵ -caprolactone) in Poly(ϵ -caprolactone) and Poly(vinyl methyl ether) Mixtures

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ABSTRACT: The morphological development and crystallization behavior of poly(ϵ -caprolactone) (PCL) in miscible mixtures of PCL and poly(vinyl methyl ether) (PVME) were investigated by optical microscopy as a function of the mixture composition and crystallization temperature. The results indicated that the degree of crystallinity of PCL was independent of the mixture composition upon melt crystallization because the glass-transition temperatures of the mixtures were much lower than the crystallization temperature of PCL. The radii of the PCL spherulites increased linearly with time at crystallization temperatures ranging from 42 to 49°C. The isothermal growth rates of PCL spherulites decreased with the amount of the amorphous PVME compo-

nents in the mixtures. Accounting for the miscibility of PCL/PVME mixtures, the radial growth rates of PCL spherulites were well described by a kinetic equation involving the Flory–Huggins interaction parameter and the free energy for the nuclei formation in such a way that the theoretical calculations were in good agreement with the experimental data. From the analysis of the equilibrium melting point depression, the interaction energy density of the PVME/PCL system was calculated to be -3.95 J/cm^3 . © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 615–622, 2007

Key words: poly(ϵ -caprolactone); poly(vinyl methyl ether); crystallization; mixtures

INTRODUCTION

Polymer blending is a useful and economical way of developing new materials with combined properties.¹ Polymer blends have been used in a wide variety of fields, including everyday materials, transportation, construction, space flight, and biomedical devices. Theoretical and experimental studies of the crystallization kinetics of miscible mixtures of crystalline and amorphous polymers have drawn more and more attention^{2–19} for the past few decades.

The crystallization of polymers from miscible mixtures of semicrystalline and amorphous components is a complicated process. To address the crystal growth in polymers, several theoretical models^{20–24} have been developed. The theoretical framework was

first suggested by Turnbull and Fisher²¹ and then modified on a molecular basis by Hoffman and coworkers.^{22–24} Under optical microscopy, the measured values of the spherulitic growth rate (G) and crystallization temperature were successfully described by the nucleation theory of Turnbull and Fischer and by the calculation of the free energy of critical nucleus formation on the crystal surface (ΔF_m^*) based on the work of Flory and Mandelkern. In our previous work,^{21,25} the decrease in G of the crystallizable component upon the addition of a miscible noncrystallizable polymer was attributed to the increase/decrease of the free energy for the formation of a critical nucleus on the crystal surface and the increase/decrease of the mobility of both the crystalline and amorphous phases. As a matter of fact, there are various factors contributing to G , such as the mixture composition, preparation routine, molecular weight, crystallization temperature, melting temperature, and glass-transition temperature (T_g). Of all of them, the major factor that affects the growth rate most in any miscible mixtures is T_g . T_g is related to the mobility of the crystallizable unit, along with the energy required for the transport of crystallizable chain components from the melt to the liquid–crystal interface.

Poly(ϵ -caprolactone) (PCL) is a kind of semicrystalline polyester with biodegradability. It has been reported to be miscible with different polymers.^{14,15,18,26–29} The crys-

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tallization kinetics of PCL in miscible mixtures with other amorphous polymers have also been extensively studied.^{12–19} A PCL/poly(vinyl methyl ether) (PVME) mixture has been chosen as a reference crystalline/amorphous system for our study. This binary system exhibits a comparatively lower critical solution temperature than other systems, which is about 473 K.²³ Below this temperature, the two components, that is, PCL and PVME, are miscible over the entire composition range^{27,28} in the amorphous state. In the literature, the crystallization kinetics of the crystallizable polymer in binary miscible mixtures, for which T_g of the noncrystallizable polymer is higher than the crystallization temperature of the crystallizable one, have been widely investigated. However, there have thus far been few reports in which T_g of the amorphous component, such as PVME, is lower than the crystallization temperature of PCL. When T_g of the amorphous component is higher than the crystallization temperature of the crystallizable component, the mobility of the crystallizable components is reduced in the melt, and as a result, G is expected to decrease with its composition in the binary mixture.³⁰ In contrast, if polymers crystallize from miscible mixtures in which T_g of the amorphous component is lower than the crystallization temperature of the crystalline component, how will the crystallization behavior be affected? This article provides deeper insights into the crystallization kinetics of amorphous/crystalline mixtures by looking into the crystallization behavior of PCL against amorphous PVME components.

EXPERIMENTAL

Materials

The PCL used in this work was a commercial product of Polysciences, Inc. (Warrington, PA). The weight-average and number-average molecular weights determined by gel permeation chromatography were 22,000 and 11,300, respectively, and their ratio was 1.93. The melting temperature of PCL was about 60°C. T_g of PCL was about –60°C. The PVME here was also supplied by Polysciences as a 50 wt % water solution and dried under a vacuum at 50°C to a constant weight before the preparation of the mixtures. T_g of PVME was about –25°C.

Preparation of the mixtures

Mixtures of PCL and PVME were made by solution casting. PCL and PVME were dissolved in toluene at room temperature, yielding a 2 wt % solution. The solutions were stirred continuously for at least 24 h at room temperature and subsequently poured onto a Petri dish. The solution-cast samples were obtained after the evaporation of the solvent at room temperature for 1 week and then kept in a vacuum for 2 days. The

melt-crystallization samples were obtained as follows. The solution-cast mixtures were first heated to 100°C and maintained at this temperature for 10 min and then rapidly cooled to the pre-stated crystallization temperature; the sample crystallized isothermally at this temperature for at least 1 week in a vacuum.

Characterization

Polarizing optical microscopy

A polarizing optical microscope (DMR, Leica, Wetzlar, Germany) equipped with a JVC (Yokohama, Japan) TK-C1381 color video camera and a Linkam (Waterfield, UK) CSS 450 optical hot stage (temperature-controlled within $\pm 0.2^\circ\text{C}$) were used to observe the isothermal crystallization process of the PCL/PVME mixtures. The solution-cast samples were first annealed at 100°C (above the melting point of pure PCL) for 10 min and then cooled to the pre-stated crystallization temperature with a $-30^\circ\text{C}/\text{min}$ cooling rate. The sizes of the growing spherulites were followed with digital images taken at appropriate intervals of time with an image processor (from Linkam and Leica).

Differential scanning calorimetry (DSC)

Thermal analysis experiments were carried out in a PerkinElmer DSC-7 apparatus in a dry nitrogen atmosphere. The temperature and heat flow were calibrated with an indium standard. The sample weight used in the DSC experiments was about 5–10 mg. All samples were heated to 100°C with a $10^\circ\text{C}/\text{min}$ heating rate, and the first scan was recorded. For measurements of T_g 's, the solution-cast samples were heated from room temperature to 100°C with a heating rate of $10^\circ\text{C}/\text{min}$ and there maintained for 3 min to remove the thermal history and ensure complete melting of the PCL crystals; then, they were quickly cooled to -70°C with a cooling rate of $100^\circ\text{C}/\text{min}$ to prevent crystallization and at last were heated to room temperature with a heating rate of $10^\circ\text{C}/\text{min}$, and the last scan was recorded.

RESULTS AND DISCUSSION

Miscibility and melting behavior

Generally, the miscibility between two components is investigated with DSC. According to the conventional DSC measurements, a mixture is often regarded as being miscible when it exhibits a single T_g between the T_g 's of the pure components and immiscible (or partially miscible) when two distinct T_g 's are detected. From Figure 1, it is evident that PCL is miscible with PVME when they are in the amorphous state because only a single T_g appears, which is the midpoint of the specific heat increment on heating as observed from the

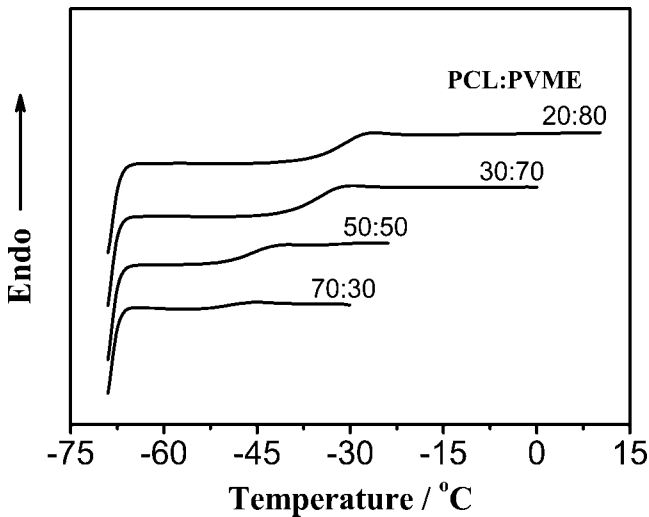


Figure 1 DSC heating thermograms of PCL/PVME mixtures for the measurements of the T_g values.

thermograms. T_g of this binary mixture also increases with increasing content of PVME. The dotted line in Figure 2 is drawn on the basis of the Fox equation:³¹

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \quad (1)$$

where w_i and $T_{g,i}$ are the weight fraction and glass-transition temperature of the i th component, respectively. Figure 2 shows clearly that the experimental data are consistent with the theoretical results, and this indicates that the interaction between the components in this mixture is weak.

Figure 3(a,b) displays the DSC thermograms of PCL/PVME mixtures prepared by the solution-cast-

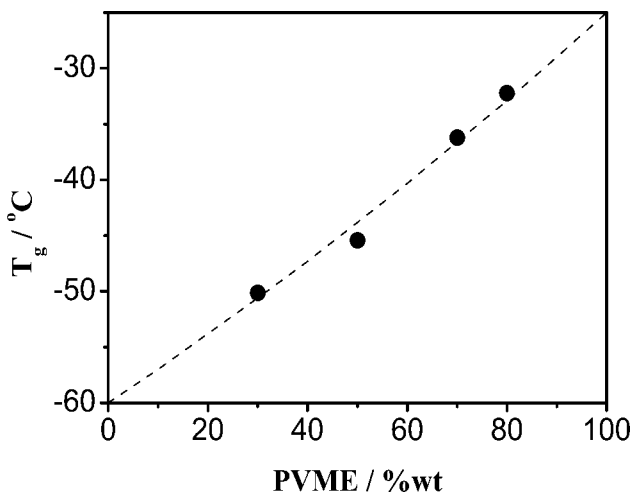


Figure 2 T_g values of PCL/PVME mixtures as a function of the PVME contents in the mixtures. The dashed line is plotted according to the Fox equation, and the circles represent experimental data.

ing and melt-crystallization methods, respectively. Figure 3(a,b) clearly shows that the melting points decrease with an increasing content of amorphous PVME because these mixtures are situated in the region of the miscibility window.^{7,27}

From a thermodynamic point of view, the equilibrium melting temperatures of PCL/PVME binary miscible mixtures are depressed with increasing contents of PVME because the chemical potential decreases. This phenomenon can frequently be used to evaluate the polymer-polymer interaction parameter between the mixed components. Therefore, it can be calculated according to the Flory-Huggins approximation:³²

$$\frac{1}{T_m^0} - \frac{1}{T_m^0} = -\frac{RV_{2u}}{\Delta h_u V_{1u}} \left[\frac{\ln \phi_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1} \right) \phi_1 \right] - \frac{RV_{2u}}{\Delta h_u V_{1u}} \chi_{12} \phi_1^2 \quad (2)$$

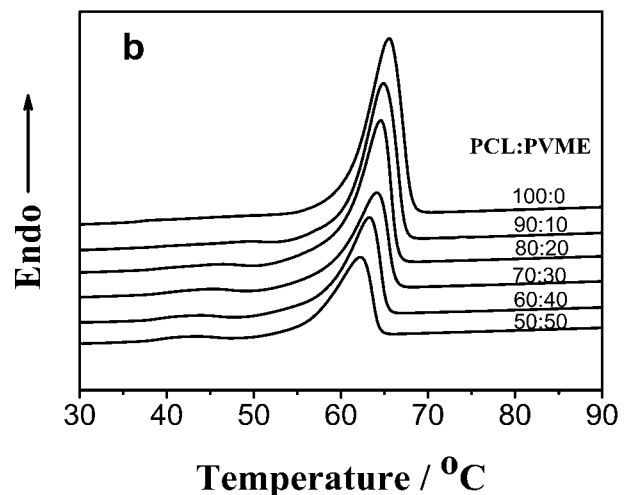
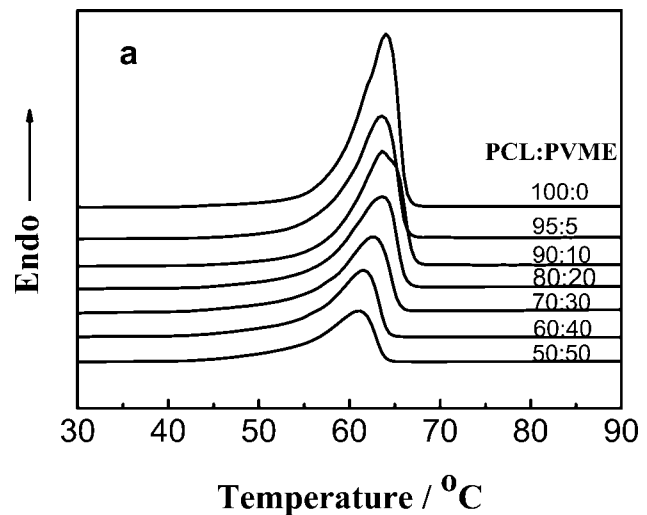


Figure 3 DSC curves of PCL/PVME mixtures prepared by (a) solution casting and (b) melt crystallization at a heating rate of $10^\circ\text{C}/\text{min}$.

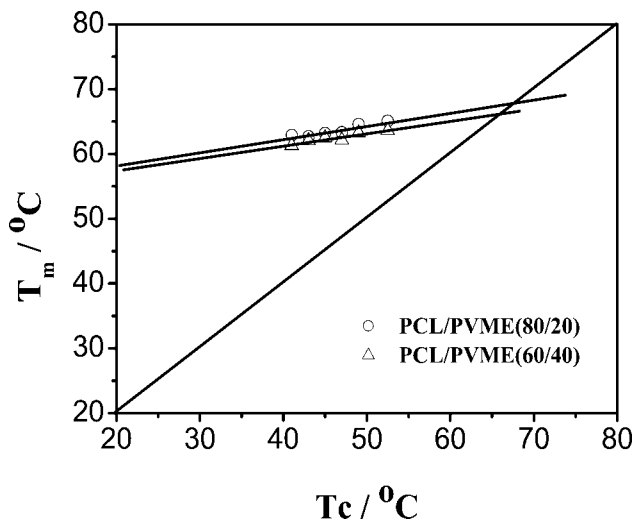


Figure 4 Hoffman-Weeks plots for the PCL/PVME mixtures (T_c = crystallization temperature, T_m = melting temperature).

where subscripts 1 and 2 refer to the amorphous polymer and the crystalline polymer, respectively; χ_{12} is the Flory-Huggins interaction parameter; R is the gas constant; V_{iu} is the molar volume of the polymer repeat unit; m_i is the degree of polymerization; ϕ_i is the volume fraction; Δh_u is the enthalpy of fusion per mole of the monomer of the crystallizable component with volume fraction ϕ_2 at temperature T ; and T_m^0 and T_m^{0r} are the equilibrium melting temperatures of the mixture and pure PCL, respectively (for the mixtures of PCL/PVME, the melting point generally increased with the crystallization temperature, as shown in Fig. 4). The extrapolation of these data in a manner outlined by Hoffman and Weeks³³ yields the equilibrium melting point. χ_{12} can be written as follows:

$$\chi_{12} = \frac{BV_{1u}}{RT} \quad (3)$$

where B is the interaction energy density of the two polymers.

For a high molecular weight, m_1 and m_2 are very large in comparison with 1. Taking into account these considerations, eq. (2) therefore can be expressed as follows:

$$T_m^{0r} - T_m^0 = \Delta T_m^0 = -B \frac{V_{2u}}{\Delta h_u} T_m^{0r} \phi_1^2 \quad (4)$$

As can be found from eq. (4), a straight line is obtained upon the plotting of ΔT_m^0 against ϕ_1^2 , as shown in Figure 5. The slope of the line is 14.60. With the constants $\Delta h_u = 1.63 \times 10^4$ J/mol,^{30,32} $V_{2u} = 107.55 \times 10^{-6}$ m³/mol, and $V_u = 76.32 \times 10^{-6}$ m³/mol and the slope, the value of B in this work is equal to -3.95 J/cm³. Comparing the values of B for PCL/PVME mixtures obtained in this work with the B value for phenoxy/

PCL ($B = -2.41$ cal/cm³ = -10.74 J/cm³) given by de Juana and Cortazar³⁴ and for poly(vinyl phenol-co-methyl methacrylate)/poly(ethylene oxide) (PVPh-co-PMMA/PEO) ($B = -29.23$ J/cm³) given by Kuo and Chang,³⁵ we find that the strength of the intermolecular interaction corresponding to the PCL/PVME mixtures is weaker than that corresponding to phenoxy/PCL and PVPh-co-PMMA/PEO mixtures because there are strong hydrogen-bond interactions in the two systems. On the basis of this experimental evidence, the interaction parameter is negative, so the two polymers are miscible, and this is in agreement with ref. 36. In this work, according to eq. (3), the value of χ_{12} is equal to -0.11 at 70.2°C.

Crystallinity

The weight percentage crystallinity of PCL (X_C) in mixtures is an important parameter for this study. It is calculated from the measured fusion heat with the following relation:

$$X_C = \frac{\Delta H_f}{w_A \times \Delta H_f^0} \times 100\% \quad (5)$$

where ΔH_f is the apparent heat of fusion per gram of the mixtures, w_A is the concentration of PCL (wt %) in the polymer mixtures, and ΔH_f^0 is the thermodynamic heat of fusion per gram of completely crystalline PCL and is assumed to be 136.08 J/g.^{37,38} Figure 6 shows the effect of the mixture composition on the crystallinity percentage of samples prepared by melt and solution techniques. It is clearly found that the degree of crystallinity of PCL in the solution-cast samples and in melt-crystallization samples remains almost constant, regardless of the mixture composition. The crystallinity development of PCL is known to be sensitive

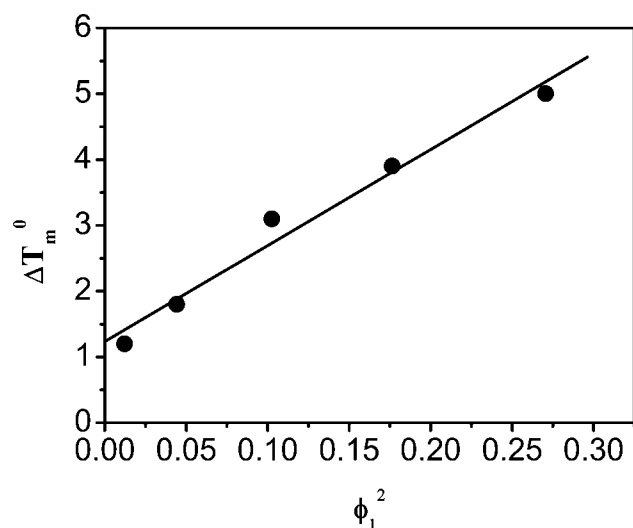


Figure 5 Plots of ΔT_m^0 versus ϕ_1^2 for PCL/PVME mixtures.

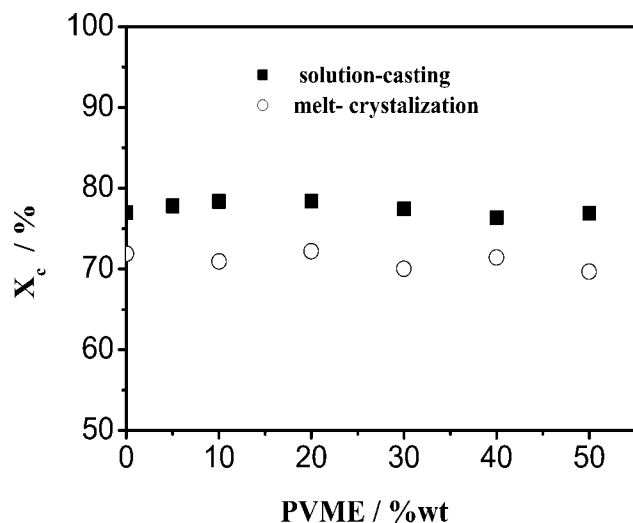


Figure 6 X_C of PCL in the mixtures as a function of the weight percentage of PVME.

to the preparation methods. Usually, the entire crystallization process is easy in solution-cast samples because the movement of macromolecular chains is relatively free; that is, the PCL mobility is allowed because of the presence of the solvent during the sam-

ple drying. For the melt-crystallized specimens, the T_g of a mixture is generally related to the mobility of the crystallizable PCL. Although the mixture T_g increases as the PVME content in the mixtures is increased, it is much lower than the crystallization temperature of PCL. Because T_g of PVME is lower than the crystallization temperature of PCL, the crystallizable component PCL remains mobile during melt crystallization. When we compare the mixture in this work with a PCL/SAN system, we find that T_g of poly(styrene-co-acrylonitrile) (SAN) is higher than the crystallization temperature of PCL, and this means that T_g of PCL/SAN is higher than or close to the crystallization temperature, so the crystallization process for a PCL/SAN binary mixture may be interrupted, and the crystallinity of PCL decreases rapidly with higher SAN concentrations and drops to zero in the mixture containing more than 40% SAN.^{39,40}

Spherulitic morphology and crystallization kinetics

Figure 7 presents polarized light optical micrographs of PCL spherulite growth from the melt of the pure material and the PCL/PVME (80/20) mixture during the isothermal crystallization at the indicated temper-

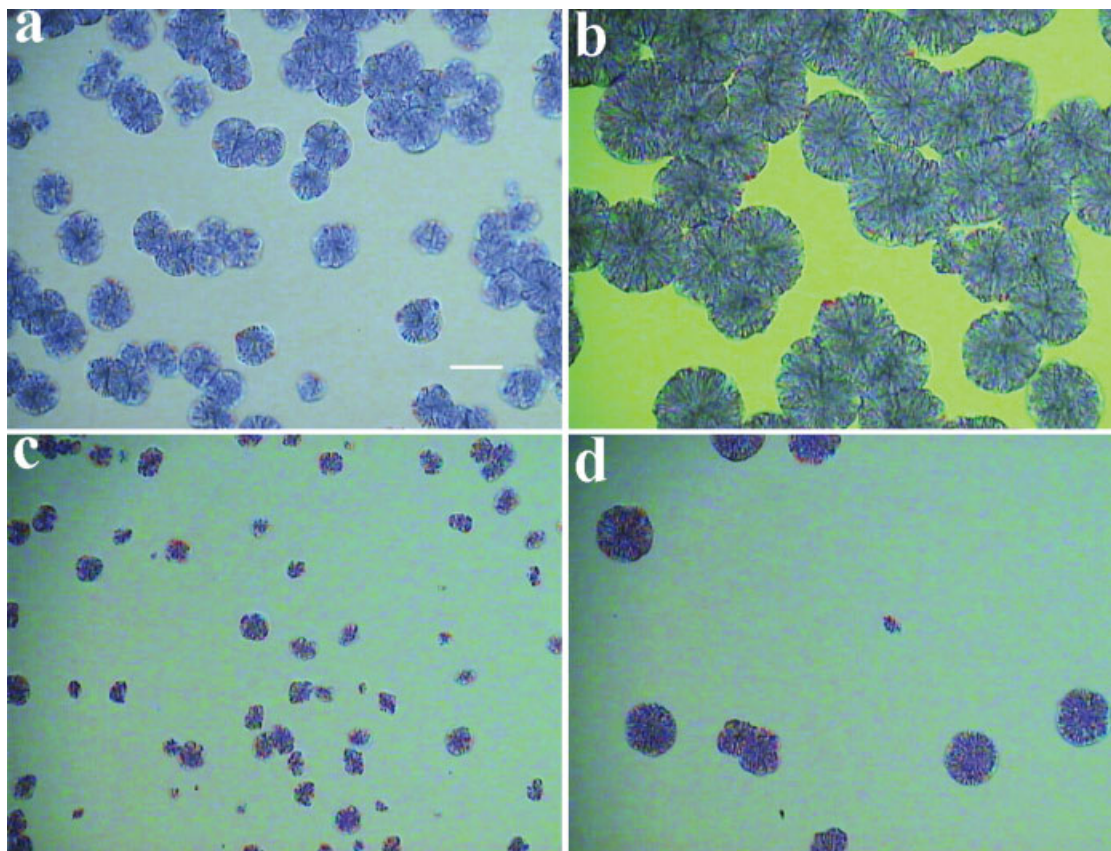


Figure 7 Polarized light micrographs for (a,b) pure PCL and (c,d) a PCL/PVME (80/20) mixture crystallized from the melts at crystallization temperatures of (a,c) 43 and (b,d) 48°C and at crystallization times of (a,c) 4 and (b,d) 35 min. The scale bar corresponds to 100 μ m. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ature. The spherulites of the mixtures do not display a clear black cross, and the growth is radial; at the same time, the nucleation number decreases with the crystallization temperature and the content of amorphous phase PVME increasing.

In Figure 8, the spherulitic radius is plotted against the crystallization time at various crystallization temperatures for pure PCL and the PCL/PVME (80/20) mixture. The radius of the PCL spherulites increases linearly with the crystallization time up to the impingement of the spherulites. The isothermal radial G values of the PCL spherulites for all the measured crystallization temperatures and compositions investigated were obtained from the slopes of similar lines. Figure 9 shows a summary of all the spherulitic isothermal growth rates measured as a function of the crystallization temperature for the PCL/PVME mixtures with different PCL contents. The crystallization

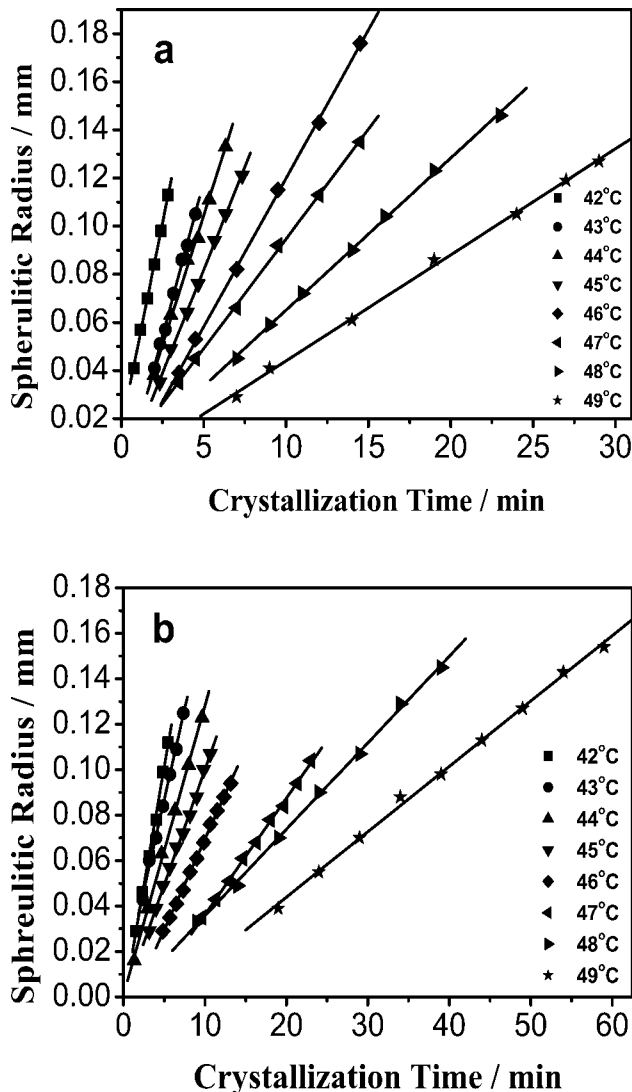


Figure 8 Variation in the spherulite radius with the crystallization time for (a) pure PCL and (b) a PCL/PVME (80/20) mixture measured at different crystallization temperatures.

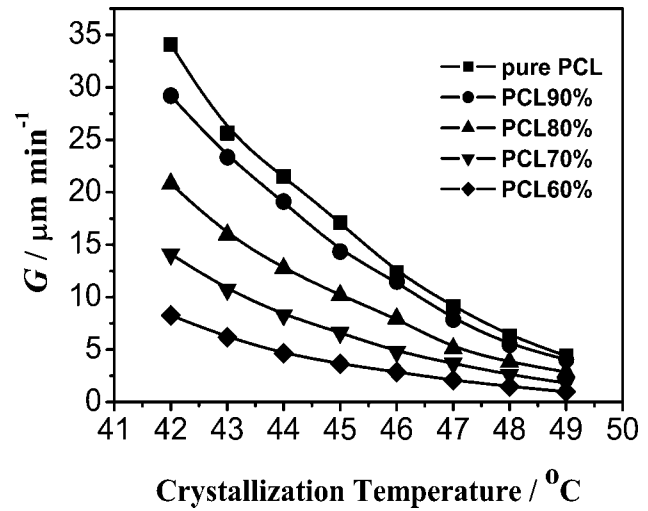


Figure 9 Dependence of G on the crystallization temperature for pure PCL and for PCL/PVME mixtures.

temperature dependence of G for the mixtures is very similar to that for pure PCL. However, the growth rate is depressed with increasing PVME. In comparison with a pure system, the dilution of a polymer should influence the free energy of nucleus formation and the transport process of the crystallizable polymer chain to the growing front of the crystal.^{19,41}

The experimental growth-rate data are analyzed by a modified version of the phenomenological theory of nucleation of Turnbull and Fisher.^{21,23} For the miscible PCL/PVME mixtures, G of the crystal can be described in terms of the following equation:

$$G = \phi_2 G_0 \exp \left[-\frac{\Delta E}{R(T - T_g + C)} \right] \exp \left(\frac{-\Delta F_m^*}{k_b T} \right) \quad (6)$$

where G_0 is a constant that depends on the regime of crystallization and is assumed equal to that of the

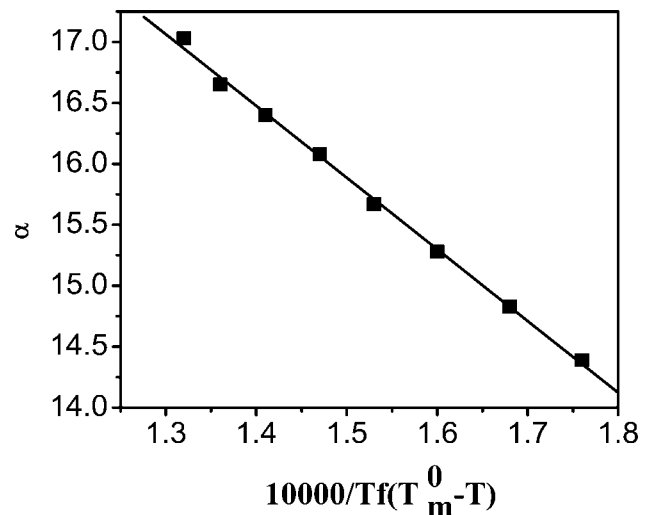


Figure 10 Plot of α versus $1/Tf(T_m^0 - T)$.

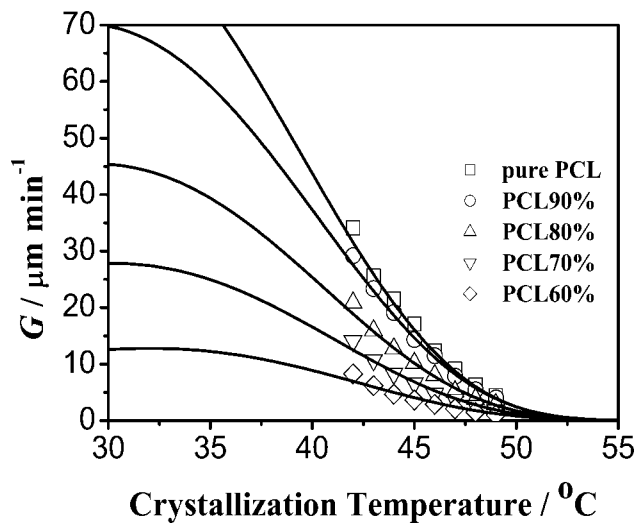


Figure 11 Curves of G with the crystallization temperature calculated with eq. (9) (shown by the solid line).

pure semicrystalline polymer; ϕ_2 is the volume fraction of the crystallizable component (PCL); ΔE is the activation energy necessary to achieve the transport of segments across the liquid–solid interface, which, because of the local nature of this term, is the same as that of the pure PCL^{7,42}; T_g is the glass-transition temperature of the mixture; C is a constant that varies from one polymer to another (in this study, the value of 51.6°C was found to fit all the data); T is the temperature of crystallization; and k_b is the Boltzmann constant. This equation produces the observed bell-shaped curve for the growth rate as a function of temperature. The growth rate is nucleation-controlled at low undercooling and diffusion-controlled at high undercooling.

Using a lattice treatment, Flory⁴³ and Mandelkern⁴⁴ evaluated ΔF_m^* for the case of semicrystalline polymers in the presence of a low-molecular-weight diluent. Their treatment can be extended easily to the case of a polymer–polymer mixture as follows:

$$\Delta F_m^* = \frac{2b\sigma\sigma_e}{\Delta h_{if} \left[1 - \frac{T}{T_m^0} - \frac{RT\chi_{12}}{\Delta h_{if}} \frac{V_{2u}}{V_{1u}} (1 - \phi_2)^2 \right]} \quad (7)$$

where V_{iu} is the molar volume of component i , b is the thickness of the nucleus ($b = d_{110}$), and $\sigma\sigma_e$ is the product of the lateral and fold surface free energies. The temperature dependence of Δh_{iu} is embedded in parameter f , which is described as follows:

$$f = \frac{2T}{(T + T_m^0)} \quad (8)$$

where T_m^0 is the equilibrium melting temperature.

By the substitution of ΔF_m^* into eq. (6), the crystal growth rate for the miscible PCL/PVME mixtures can

be represented by the following equation:

$$G_m = \phi_2 G_0 \exp \left[-\frac{\Delta E}{R(T - T_g + C)} \right] \times \exp \left[-\frac{2b\sigma\sigma_e}{k_b T \Delta h_{if} f \left(1 - \frac{T}{T_m^0} - \frac{RT\chi_{12}}{\Delta h_{if}} \frac{V_{2u}}{V_{1u}} \chi_{12} (1 - \phi_2)^2 \right)} \right] \quad (9)$$

The growth rate data for all the mixtures are calculated according to eq. (9). The energy required to transport segments across the solid–liquid interface, ΔE in eq. (6), is usually estimated with the Williams–Landel–Ferry empirical relation for the temperature dependence of the viscosity,^{3,45} in our study, ΔE is 17,238.1 J/mol. G for the mixtures can be described by eq. (9); for a pure crystallizable polymer, the relationship can be modified as follows:

$$G_m = G^0 \exp \left[-\frac{\Delta E}{R(T - T_g + C)} \right] \times \exp \left[-\frac{2b\sigma\sigma_e}{k_b T \Delta h_{if} f \left(1 - \frac{T}{T_m^0} \right)} \right] \quad (10)$$

Then

$$\ln G_m + \frac{\Delta E}{R(T - T_g + C)} = \ln G_0 - \frac{2b\sigma\sigma_e T_m^0}{k_b \Delta h_{if}} \times \frac{1}{Tf(T_m^0 - T)} = \alpha \quad (11)$$

On the basis of the former experimental data and eq. (10), a straight line is obtained α is plotted versus $\frac{1}{Tf(T_m^0 - T)}$, as shown in Figure 10. From the intercept of the line, $\ln G_0 = 24.71$ or $G_0 = e^{24.71}$ $\mu\text{m}/\text{min}$ is obtained, and the slope, equal to -58824.27 , can be described by the following relation:

$$\text{Slope} = \frac{2b\sigma\sigma_e T_m^0}{k_b \Delta h_{if}} \quad (12)$$

The product $\sigma\sigma_e$ is calculated with $b = 0.438$ nm.¹² The result is $\sigma\sigma_e = 444.28 \times 10^{-6}$ (J/M²)². The value of $\sigma\sigma_e$ for all the mixtures is similar to that of the pure crystallizable component,^{19,41} so we assume that the product is independent of the composition in this work.

All the thermodynamic parameters are obtained as before; the curves of G of the mixtures, calculated with eq. (9), are presented in Figure 11. As can be seen more clearly from this plot, the experimental growth rates coincide quite well with the calculated curves, except for those at lower crystallization temperatures, at which the experimental growth rates increase a little above the theoretical curves of the growth rates.

CONCLUSIONS

A study on PCL crystallization behavior in PCL/PVME mixtures has been performed over a wide

range of crystallization temperatures and for several compositions. The degree of crystallinity of PCL in the mixtures remains almost constant, regardless of the mixture composition during PCL crystallization from melt and solution casting, because T_g of the mixture is lower than the crystallization temperature of PCL. The temperature dependence of the spherulite growth rates is very similar to that for homopolymers, and the growth rates decrease with an increasing amount of amorphous polymer PVME in the mixtures. On the basis of the modified phenomenological theory of nucleation, the relationship between G and the crystallization temperature has been theoretically calculated; the experimental growth rates coincide quite well with the calculated curves. In light of these results, the noncrystallizable component PVME does not affect the crystallization behavior of PCL in the PCL/PVME mixture from a thermodynamic point of view, but from the viewpoint of kinetics, the growth rates are restrained because of the presence of PVME for dilution. In addition, B has been obtained with the melting point depression equation.

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