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Kinetics of Spherulitic Growth of Poly(pivalolactone) in Blends with Poly(vinylidene fluoride-*co*-tetrafluoroethylene): Effect of Specific Interactions on the Thermodynamic and Kinetic Secondary Nucleation Parameters

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ABSTRACT: The kinetics of spherulitic growth of α-phase poly(pivalolactone) (PPVL) in blends with poly(vinylidene fluoride-*co*-tetrafluoroethylene) (P(VF_2-TFE)) has been investigated as a function of blend composition and crystallization temperature by hot-stage polarized optical microscopy and analyzed by the Lauritzen−Hoffman (LH) secondary nucleation theory. The composition dependence of the equilibrium melting temperature of α-phase PPVL was determined directly from the analysis of spherulitic growth rate data evaluated at various crystallization temperatures between 169.4 and 217.4 °C. The estimated equilibrium melting temperatures were analyzed by the Nishi−Wang method to yield a negative Flory−Huggins interaction parameter ($\chi_{F-H} = -0.06 \pm 0.03$). Analysis of the composition dependence of the nucleation constants, K_g, in crystal growth regimes II and III suggests that the PPVL crystal/melt lateral interfacial free energy, σ, decreases markedly with increasing P(VF_2-TFE) concentration in the blends. The present results were examined in light of conclusions drawn from previous studies of PPVL/PVF_2 blends and allowed us to state that the composition dependence of K_g and σ for α-phase PPVL is unequivocally a function of the strength of the specific interactions between the blend components. These observations are rationalized through arguments based on the minimization of the free energy of demixing and an increase in the conformational entropy of chains adsorbed at the melt/crystal interphase (i.e. an increase in crystal/melt lateral interfacial thickness) with an increase in the strength of the specific interactions.

Introduction

Recently, we reported[1] a detailed study of the temperature dependence of spherulitic growth rates of α-phase PPVL in miscible blends with PVF_2. A new approach was used to assess the composition-dependent equilibrium melting temperature, T_m, nucleation constants, K_g, and the surface free energy product, $\sigma\sigma_e$, of α-phase PPVL crystals in blends with PVF_2 directly from spherulitic growth rate data using the Lauritzen−Hoffman (LH) kinetic theory.[2−4] All these quantities were found to decrease with increasing PVF_2 concentration in the blends. The equilibrium melting temperature of α-phase PPVL crystals formed in the absence of the PVF_2 diluent, estimated with this new approach, was in excellent agreement with that derived in an earlier study[7] using the Gibbs−Thomson−Tammann method. The blend composition dependence of the PPVL α-phase equilibrium melting temperature obtained by this new approach was analyzed using the Nishi−Wang treatment[5] to yield a Flory−Huggins parameter, $\chi_{F-H} = -0.13 \pm 0.05$, of magnitude which is consistent with values reported for PVF_2/PMMA blends.[5] Independent evaluation of the depression in the PPVL equilibrium melting temperature for various blend compositions using the Hoffman−Weeks approach yielded results that were consistent with these obtained by the kinetic method.[1] These observations indicate that one can determine reasonably well the equilibrium melting temperature through an examination of the temperature dependence of crystal growth rate data.

The mere fact that a reasonable Flory−Huggins interaction parameter can be obtained indirectly through the fitting of crystal growth rate data to the LH theory suggests that this theory, which was developed for homopolymers, is also appropriate for crystal growth in single-phase mixtures. In this previous study,[1] it was also concluded that the melt/crystal lateral interfacial free energy, σ, exhibits a dramatic blend composition dependence (decreasing from 29 ± 3 for pure PPVL[6,7] to 7 ± 1 erg cm^{-2} for the 10/90 PPVL/PVF_2 blend). The variation of σ with blend composition was first tentatively interpreted on the basis of a recent model[8] correlating the lateral melt/crystal interfacial free energy and the polymer characteristic ratio, C_∞, invoking the departure of the melt from the θ state and the related swelling of the PPVL coils by the PVF_2 diluent. If the change in σ is to be totally attributed to the change in conformational entropy of the PPVL in the melt state through swelling, then the required value of the chain expansion coefficient should be around $\alpha = 2.0$ for the 10/90 PPVL/PVF_2 blend. Since this value is clearly too high to be credible,[9] one is led to propose that both the chain conformation in the liquid and in the state of physical adsorption at the crystal−liquid interphase must be affected by mixing and specific interactions. A qualitative argument was then proposed to discuss the magnitude of the lateral surface free energy, σ, in terms of the strength of the molecular interactions between the two blend components. Since crystallization in a mixture occurs through a demixing process and since the activated state for the secondary nucleation event is generally viewed as a section of a polymer chain in a state of physical adsorption at the crystal growth front,[2,8] the minimization of the free energy barrier to nucleation will require the extent of demixing and the change in chain conformation entropy upon physical adsorption onto the growth front to be minimized. It

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was speculated that such conditions are realized by increasing the thickness of the crystal−liquid interphase (i.e. by allowing the adsorbed chain larger excursions away from the growth front where it can interact more freely with segments of the second blend component). This very qualitative model predicts that the more favorable the molecular interactions between blend components, the thicker the interfacial region. The goal of the present study is to investigate the latter prediction by considering the spherulitic growth of PPVL crystals in blends with P(VF_2-TFE) and by comparing the magnitude of the lateral melt−crystal interfacial free energy measured for PVF_2 and for P(VF_2-TFE) blends. Blends of PPVL with the latter polymeric diluent should be characterized by a less negative χ_{F-H}, since in contrast with the vinylidene fluoride repeat units, the tetrafluoroethylene units do not form hydrogen bonds with the PPVL ester groups. One therefore predicts that the lateral melt−crystal interfacial free energy for α-phase PPVL crystals should be the largest in blends with PVF_2 and the lowest for pure PPVL. Intermediate values should be observed in blends with the P(VF_2-TFE) copolymer.

According to the LH theory,[2−4] the temperature-dependent isothermal spherulitic growth rate, G, is given by

$$G_i = G_i^\circ \exp\left(\frac{-U^*}{R(T_x - T_\infty)}\right) \exp\left\{\frac{-K_{g(i)}}{T_x \Delta T\ f(T_x)}\right) \qquad (1)$$

where *i* represents the crystallization regime I, II, or III. The preexponential factor G_i° is weakly temperature dependent and is generally treated as a constant within each regime. The first exponential term $\exp[-U^*/R(T_x - T_\infty)]$ accounts for the temperature dependence of the transport of polymer chain segments through the subcooled melt to the liquid−solid interface,[10] where U^*, is generally taken to be 1500 cal/mol and T_∞, generally taken as $T_g - 30$ K, is the temperature at which the transport of segments across the liquid−solid interface becomes infinitely slow. Although the values of U^* and T_∞ for PPVL need not be identical to these conventional values, it has been shown[6] that when crystallization takes place at temperatures far above the glass transition temperature, T_g, the uncertainty in the transport term due to uncertainties in U^* and T_∞ values, have a negligible effect on the crystal growth rate (note that for the study of PPVL crystal growth in blends with PVF_2 or P(VF_2-TFE), $T_{g(PPVL)} \approx -3$ °C, $T_{g[P(VF_2\text{-}TFE)]} \approx T_{g(PVF_2)} \approx -40$ °C, while $T_x = 170-217$ °C). The second exponential term (secondary nucleation term) $\exp[-K_{g(i)}/T_x\Delta T\ f(T_x)]$ is a measure of the probability of formation of a thermodynamically stable secondary surface nucleus. The undercooling, $\Delta T = T_m - T_x$, is the temperature difference between the equilibrium melting temperature T_m and crystallization temperature T_x, and $f(T_x) = 2T_x/(T_m + T_x)$ is a small empirical correction factor accounting for the temperature dependence of the free energy of crystallization. The nucleation constant, K_g, is given by

$$K_{g(i)} = \frac{2 j_i b_0 \sigma \sigma_e T_m}{k \Delta h_f^\circ} \qquad j_{I,III} = 2 \qquad j_{II} = 1 \qquad (2)$$

where b_0 is the monomolecular layer thickness in the growth direction (0.574 nm), *k* the Boltzmann constant, Δh_f° the enthalpy of fusion per unit volume of a perfect and infinitely large crystal at its melting temperature (183.7 J cm^{-3}).

In practice, eq 2 is often written in logarithmic form:

$$\ln G_i + \frac{U^*}{R(T_x - T_\infty)} = \ln G_i^\circ - \frac{K_{g(i)}}{T_x \Delta T\ f(T_x)} \qquad (3)$$

Therefore, a plot (thereafter called the LH plot) of the left-hand side of eq 3 vs $1/(T_x\Delta T\ f(T_x))$ can be used to determine the nucleation constant $K_{g(i)}$ from the slope of the straight line in each regime, provided that the equilibrium melting temperature, T_m, is known and a set of growth rate data as a function of crystallization temperature is available.

Once the $K_{g(i)}$ values are obtained, $\sigma\sigma_e$ can be calculated using eq 2 provided that Δh_f° and b_0 are known. In many studies, the value of T_m is not known with sufficient accuracy, which can lead to large uncertainties in the value of $K_{g(i)}$, thus in the value of $\sigma\sigma_e$. It is therefore very important to use an accurate T_m value in the LH plot to get reasonable estimates of the crystal−melt interfacial free energy product. In a previous publication,[1] we showed that least-square fitting of the growth rate data with eq 3, allowed the determination of sufficiently accurate values of T_m.

Experimental Section

PPVL was purchased from Polysciences (lot no. 0118−006) with a viscosity average molecular weight $M_v = 250\,000$ g/mol, as measured by intrinsic viscosity in a tetrachloroethane/phenol solvent mixture by the manufacturer. The molecular weight distribution for this sample was expected to be around 2. The P(VF_2-TFE) sample was kindly provided by Atochem North America (lot no. 7062-23-D). The viscosity average molecular weights of PVF_2 and P(VF_2-TFE) were determined with a Cannon-Ubbelohde 75 J325 viscometer at 30 °C in *N*,*N*-dimethylacetamide (DMAc).

The molar concentration of the TFE repeat units in the copolymer used for this study is 3.6% (corresponding to 5.5 wt %) as measured by ^{19}F-NMR. The sample for ^{19}F-NMR measurement was prepared by dissolving the P(VF_2-TFE) sample in HPLC grade DMAc at 10 wt %. The ^{19}F-NMR measurement was performed with a Varian Unit 400 spectrometer at room temperature, and hexafluorobenzene (HFB) was used as the internal standard.[11]

The various polymer mixtures used in this study were prepared by solution blending. The received polymer pellets were first pressed into 25 to 50 μm thick films in a Carver laboratory hot press at 180 and 210 °C for P(VF_2-TFE) and PPVL, respectively, and subsequently quenched in an ice−water mixture. To minimize any polymer degradation process while ensuring complete dissolution and mixing, the PPVL film was allowed to reside in benzophenone at 180 °C for 30 min and the P(VF_2-TFE) film for 10 min under nitrogen in the absence of light and with constant stirring. The homogeneous solution was then hot filtered and precipitated in a ice−water/acetone mixture under constant stirring. The filtrate was washed with acetone several times and subsequently dried in a vacuum oven at 120 °C for 36 h. Thin films for polarized optical microscopy were prepared by melting the dry blend polymer between two glass cover slips at 260 °C for 3 min in a Linkam hot stage operated under a dry nitrogen purge. The samples were then quenched to the desired isothermal crystallization temperature, T_x, where the spherulitic growth of α-phase PPVL was followed in a Zeiss Axioplan polarizing microscope and recorded with an Ikegami ITC 510 BW video camera interfaced to a Sony video recorder. Radii of the spherulites were measured as a function of time from the Javelin monitor using an Olympus Cue Micro-300 Videocaliper. The temperature calibration of the hot stage was achieved using the melting temperature of lead and indium standards

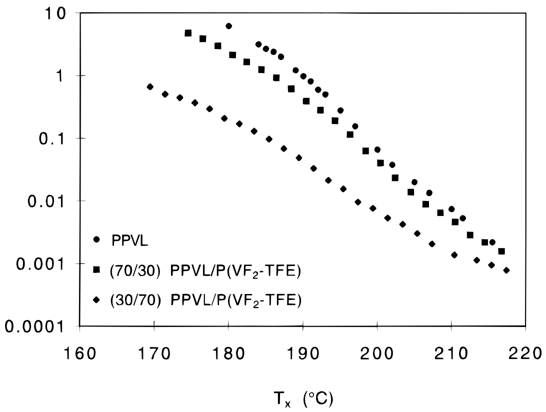

Figure 1. Plot of the isothermal spherulitic growth rate G (μm s^{-1}) vs crystallization temperature (T_x, °C) for PPVL/P(VF$_2$-TFE) blends: (●) 100/0; (■) 70/30; (▲) 30/70 w/w %.

at a very slow heating rate. The spherulitic growth rates of α-phase PPVL were estimated in the temperature range from 169.4 to 217.4 °C for 70/30 and 30/70 (wt %) PPVL/P(VF$_2$-TFE) blends. In all cases, the crystallization temperatures were high enough so that the P(VF$_2$-TFE) component remained in the liquid state. It was noted that the spherulitic growth rate remained constant until spherulites impinged, indicating that the rejection of the polymeric diluent into the interspherulitic region did not occur to a significant extent.

Results and Discussion

Since one of the major goals of this study is to compare the crystal growth behavior of PPVL in blends with P(VF$_2$-TFE) and in blends with PVF$_2$, one should first ensure that the only variable in our set of diluents is the fraction of interactive sites (i.e. VF$_2$ units) and not the diluent molecular weight. The intrinsic viscosity of P(VF$_2$-TFE) in DMAc at 30 °C was determined to be 0.99 dL/g. Using the Mark–Houwink equation, $[\eta] = kM^a$ (where the k and a values for the VF$_2$-rich copolymer were assumed to be very similar to these reported for PVF$_2$, $k = 0.000\,40$ dL/g and $a = 0.70$), the viscosity average molecular weight for the P(VF$_2$-TFE) copolymer was calculated to be 93 000 g/mol. This molecular weight is sufficiently close to that determined for the PVF$_2$ material used in the previous study ($M_v = 70\,000$ g/mol) that any significant difference in the temperature dependence of the crystal growth rate for PPVL in blends with P(VF$_2$-TFE) and PVF$_2$ cannot be attributed to diluent molecular weight effects.

Although we were initially interested in studying the crystal growth process for PPVL blended with P(VF$_2$-TFE) copolymers having different TFE contents (5, 10, and 15 wt %), we quickly realized through light-scattering studies in the melt state that only the lowest TFE content copolymer (5 wt % TFE) formed a miscible mixture with PPVL. Thus only blends of PPVL with P(VF$_2$-TFE) (95/5) are further discussed.

The α-phase PPVL growth rate vs crystallization temperature data for 100/0, 70/30, and 30/70 PPVL/P(VF$_2$-TFE) blends are plotted on a logarithmic scale as a function of T_x in Figure 1. Each growth rate data was calculated by averaging measurements over 4–12 spherulites. The average standard deviation of the growth rate data is 3.6%. Careful examination of Figure 1 suggests a clear break in the temperature dependence of the growth rate data for each blend. Such a transition, which we associate with a shift from regime III crystallization at large undercoolings to regime II crystallization at lower undercoolings, has already been reported in pure PPVL[1,6] and in PPVL/PVF$_2$ blends.[1]

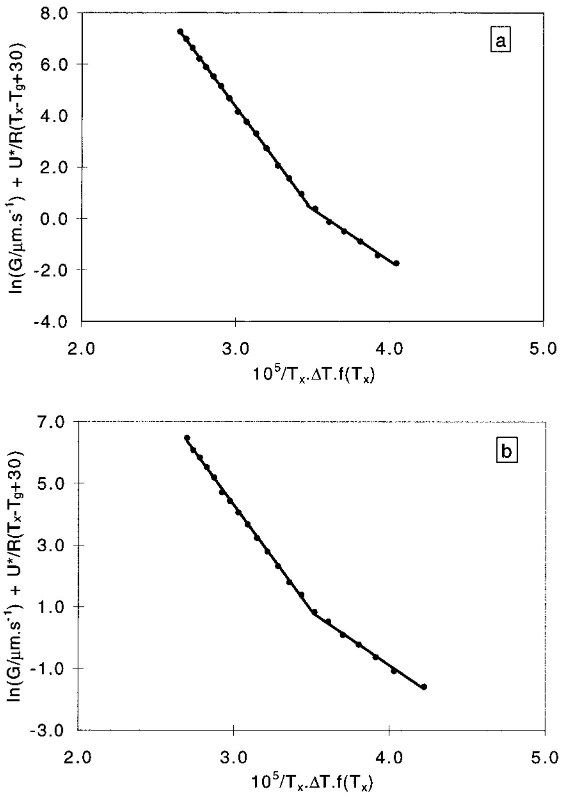

Figure 2. LH plots for (a) 70/30 and (b) 30/70 PPVL/P(VF$_2$-TFE) blends for the equilibrium melting temperatures giving the lowest variances.

Figure 2 gives the corresponding LH plot for each of the blends. The equilibrium melting temperature and the nucleation constant K_g for α-phase PPVL in each blend are obtained through a least-squared data fitting approach.[1] The plot of the variance as a function of the chosen equilibrium melting temperature is shown in Figure 3. The equilibrium melting temperature is chosen as that yielding the minimum in the variance. The value of $\sigma\sigma_e$ is calculated using eq 2 from the value of K_g obtained for the appropriate equilibrium melting temperature and is given in Table 1, along with other results from the growth rate analysis. As was observed in the case of PPVL/PVF$_2$ blends, T_m, K_g, and $\sigma\sigma_e$ decrease with increasing P(VF$_2$-TFE) concentration in the blends. However, the magnitude of the melting temperature depression observed here is not as large as observed in the case of the PPVL/PVF$_2$ system. The nature and strength of the intermolecular interactions in a single-phase mixture can be described by the Flory–Huggins interaction parameter, $\chi_{\mathrm{F-H}}$. From a thermodynamic point of view, specific interactions ($\chi_{\mathrm{F-H}} < 0$) in a polymer mixture lead to a decrease in the chemical potential of the crystallizable polymer in its liquid state, thus in a depression of the equilibrium melting temperature T_m. The widely used Nishi–Wang equation[5] relates the strength of the specific interactions, as expressed by $\chi_{\mathrm{F-H}}$, to the magnitude of the depression in the equilibrium melting temperature:

$$\frac{1}{T_{\mathrm{mb}}} - \frac{1}{T_{\mathrm{m}}} = \frac{-RV_{\mathrm{cu}}}{\Delta h^{\circ}_{\mathrm{fu}} V_{\mathrm{au}}} \chi_{\mathrm{F-H}} V_{\mathrm{a}}^{\;2} \qquad (4)$$

where T_m is the equilibrium melting temperature of the pure homopolymer (here PPVL), T_{mb} is the equilibrium melting temperature of the homopolymer crystals in the blend, $\Delta h^{\circ}_{\mathrm{fu}}$ (3.98 kcal mol^{-1}) is the heat of fusion of

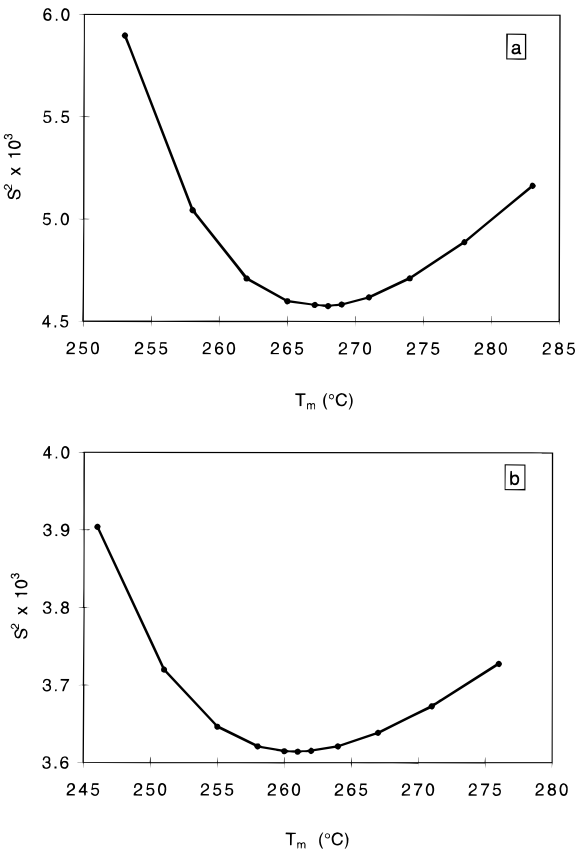

Figure 3. Plots of the variance S^2 of the least-square fits as a function of input equilibrium melting temperature, T_m for (a) 70/30 and (b) 30/70 PPVL/P(VF_2-TFE) blends.

Table 1. Kinetic and Thermodynamic Parameters for PPVL α-Phase Crystals Grown from the Melt in PPVL/P(VF_2-TFE) Mixtures

	PPVL/P(VF_2-TFE) composition		
	100/0	70/30	30/70
T_m (°C)	269 ± 3	268 ± 3	261 ± 3
T_{II-III} (°C)	203 ± 2	202 ± 2	199 ± 2
$K_{g(III)} \times 10^{-5}$ (K^2)	8.7 ± 0.7	7.3 ± 0.7	5.5 ± 0.6
$K_{g(III)}/K_{g(II)}$	2.02 ± 0.06	2.12 ± 0.04	1.74 ± 0.05
$\sigma\sigma_e$ (erg^2 cm^{-4})	1760 ± 170[a]	1440 ± 180[a]	1220 ± 190[a]
σ (erg cm^{-2})	29 ± 3[b]	24 ± 3[b]	20 ± 3[b]

[a] The $\sigma\sigma_e$ values are reported as averages over regimes II and III. The uncertainties on $\sigma\sigma_e$ were calculated from the uncertainties on K_g and from the deviation of the ratio of $K_{g(III)}/K_{g(II)}$ from 2.0. [b] To calculate σ, it was implicitly assumed that σ_e was independent of blend composition and equal to the value determined for crystal growth from pure PPVL melt.[1,5]

PPVL crystal per mole of repeat unit at T_m, V_{cu} (84.75 cm^3 mol^{-1}) and V_{au} are the molar volume per repeat unit of crystallizable (PPVL) and amorphous (P(VF_2-TFE)) polymers, and R is the gas constant. Using the values of V_{au} (40.0 cm^3 mol^{-1}) for PVF_2 and the equilibrium melting temperature for PPVL in each blend (Table 1), a plot of the left hand side of eq 4 vs the square of the P(VF_2-TFE) volume fraction in the blends can be made (see Figure 4). From the slope of the regression line, the Flory–Huggins interaction parameter was determined to be −0.06 ± 0.03 which is less negative than the value of −0.13 ± 0.05 obtained for the PPVL/PVF_2 blends.

Since the fold surface free energy, σ_e, is mainly intramolecular in origin, one will assume as before[1] that it is independent of blend composition. Such an hypothesis is supported by a number of studies which

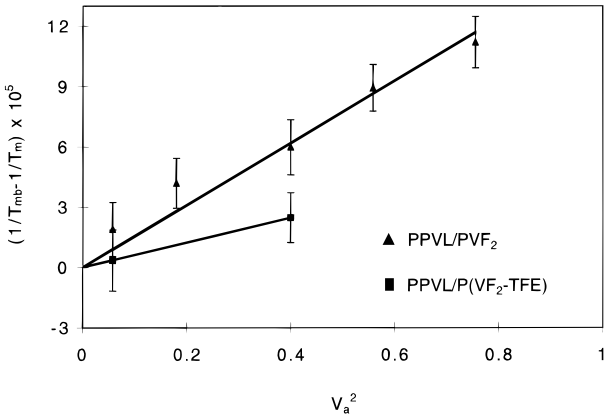

Figure 4. Plot of $1/T_{mb} - 1/T_m$ vs V_a^2 (after the method of Nishi and Wang[5]).

concluded that the polymeric diluent did not penetrate the fold melt–crystal interfacial region.[12–18] Therefore, the value of the lateral melt–crystal interfacial free energy, σ, can be calculated by assuming that the value of σ_e is independent of blend composition. Under these conditions, the lateral interfacial free energy, σ, is observed to decrease with increasing copolymer diluent concentration. One should note that if the addition of the copolymer diluent had any effect on the magnitude of σ_e for α-phase PPVL, it would certainly consist in increasing σ_e. This statement follows from the assumption that chain folding requires demixing and must lead to the decrease in the number of favorable interactions between unlike segments (i.e. the work of chain folding now also includes a demixing term besides conformational energy terms). If the demixing contribution to σ_e were to be accounted for, the magnitude of the lateral surface free energy, σ, would decrease even more dramatically with an increase in the PPVL/P(VF_2-TFE) concentration. For the sake of simplicity, we will assume that the value of σ_e is independent of composition.

To reasonably account for the rapid decrease in the value of σ with increase in the P(VF_2-TFE) composition as well as the large difference in σ values between PPVL/(VF_2-TFE) and PPVL/PVF_2 systems, we will recall the model introduced in an earlier publication[1] and summarized above in this manuscript. As pointed out in the Introduction, the physical origin of the lateral surface free energy in the kinetic description of crystal growth of a homopolymer is thought to be associated with the entropy change experienced by a portion of the polymer chain as it becomes physically adsorbed onto the crystal growth front prior to full crystallographic attachment.[8] In a miscible blend system with specific interactions, not only the state of expansion of the polymer chain in the melt away from the growth front, but also the conformational properties of the chain segments in the crystal–liquid interphase can be affected by the existence of specific interactions.

When the magnitude of σ for α-phase PPVL is compared in the PPVL/P(VF_2-TFE) and the PPVL/PVF_2 blend systems at the same composition, it is clear that it decreases more rapidly with increase in diluent concentration as the specific interactions become stronger. The value of σ must decrease as χ_{F-H} becomes more negative. Such a conclusion is in direct accord with the predictions of the qualitative model proposed earlier. That is, an increase in the lateral crystal–liquid interfacial thickness or equivalently a decrease in the extent of collapse of the crystallizing chain onto the growth front would occur during crystallization from a mixture that exhibits stronger favorable interactions. A decrease in this lateral interfacial free energy will however not result in a faster crystal growth rate from a mixed melt as the concentration of crystallizable species at the growth front will obviously be smaller for the mixed liquid than for the pure melt.

Conclusions

Using the Lauritzen−Hoffman kinetic theory of crystal growth, the equilibrium melting temperature, T_m, the lateral surface free energy, σ, of α-phase PPVL in PPVL/P(VF_2-TFE) blends have been obtained directly from spherulitic growth rate data. The α-phase PPVL equilibrium melting temperature T_m decreases with an increase in P(VF_2-TFE) concentration, as is expected for solid−liquid equilibria in single liquid phase polymer mixtures having significant specific interactions. The results obtained in this study are compared to those obtained in PPVL/PVF_2 blends. It is found that the composition dependence of T_m and σ in PPVL/P(VF_2-TFE) system is weaker than that reported for PPVL/PVF_2 blends. We proposed that the weaker specific interactions between PPVL and P(VF_2-TFE) are at the origin of this observation. The evaluation of the Flory−Huggins interaction parameter, χ_{F-H}, via analysis of the melting point depression (Nishi−Wang approach) yields a value of -0.06 ± 0.03. A model based on the correlation between melt/crystal lateral interphase thickness and strength of the specific interactions in miscible blends is used to explain the blend composition dependence of σ. Although our qualitative model for the effect of specific interactions in mixtures on the lateral crystal−liquid interfacial free energy has received further support from the present studies, it would be of interest to extend such studies to athermal polymer blends where we would predict that the lateral crystal−liquid interfacial free energy would be independent of blend composition. Such studies are in progress and will be discussed shortly.

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