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Crystallization and Melting of Isotactic Poly(3-hydroxy butyrate) in the Presence of a Low Molecular Weight Diluent

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ABSTRACT: Mixtures of isotactic bacterial poly(3-hydroxy butyrate) (PHB) with di-*n*-butyl phthalate (DBP) in the whole composition range are investigated by DSC. The glass transition (T_g) and melting temperature (T_m) of PHB/DBP mixtures regularly decrease with composition. Analysis of the melting point depression in terms of the Flory−Huggins theory yields the value $\Delta H_u = 11$ kJ/mol for the melting enthalpy of fully crystalline PHB, in excellent agreement with earlier results. The isothermal crystallization of PHB/DBP mixtures with DBP volume fraction from 0 to 0.27 is investigated over a broad temperature range (from 30 to 130 °C). The spherulite growth rate curves (G vs T_c) shift to lower temperatures with increasing DBP content, following the T_g and T_m changes. The maximum growth rate (G_{max}) does not change with composition in the range explored. Analysis of the isothermal crystallization results by the Boon−Azcue modification of the Lauritzen−Hoffman treatment yields an estimate of the product of the crystal surface free energies $\sigma\sigma_e = 12.9 \times 10^{-12}$ J²/cm⁴ that agrees with literature data and does not change with concentration in the range of DBP contents investigated.

Introduction

Natural poly(3-hydroxy butyrate), PHB, is a highly crystalline polymer, produced by a variety of bacteria as a 100% isotactic polymer. In a previous study,[1] we reported that increasing amounts of a low molecular weight diluent, di-*n*-butyl phthalate (DBP), besides gradually decreasing the glass transition temperature (T_g) of PHB, also decrease the temperature where polymer crystallization from the rubbery state (cold crystallization) occurs during a DSC heating scan. This behavior is common to both low and high molecular weight (polymeric) plasticizers[2] and indicates that the two components are miscible at molecular level. The present work analyses the dependence of the melting temperature of PHB−DBP mixtures on the amount of plasticizer over a very broad composition range (0−93 wt % DBP) and also investigates the kinetics of isothermal crystallization of PHB from the melt in PHB−DBP mixtures containing up to 25 wt % (0.27 volume fraction) DBP. For each polymer−diluent mixture a wide range of T_c's is explored, and the whole curve of the spherulite growth rate (G) as a function of crystallization temperature (T_c) is obtained.

For mixtures of polymers with low molecular weight substances very few papers[3,4] can be found in the literature that report G vs T_c results from low to high undercoolings (i.e., the whole bell-shaped curve) over a range of diluent contents. Most of the available papers on the subject either investigate single-composition polymer−diluent mixtures[5,6] over the whole T_c range or report results on several compositions but only at low undercoolings.[7,8] This work gives a contribution to fill this lacuna, by providing experimental spherulite growth rate results on polymer−diluent mixtures with changing diluent concentration, over a broad range of crystallization temperatures. PHB is an ideal model for such studies owing to its high crystallizability associated with a very low nucleation rate.

The main objectives of this study are (i) to check the applicability of the Lauritzen−Hoffman theory[9] to the spherulite growth kinetics of PHB from PHB−DBP mixtures, (ii) to discuss the melting point depression of plasticized PHB in terms of the Flory−Huggins theory,[10] (iii) to gain information on polymer−diluent interactions, and (iv) to estimate the heat of fusion of fully crystalline PHB.

Experimental Section

The PHB sample utilized in this research was an ICI commercial product (BX GV9; $M_w = 1\,140\,000$; $M_n = 350\,000$). The diluent di-*n*-butyl phthalate (purity >99%) was synthesized as previously described.[11]

PHB−DBP mixtures for calorimetric measurements were prepared directly in the DSC pans by weighing appropriate amounts of the two components; the pans were sealed and heated above PHB melting point. This procedure was adequate to promote polymer−diluent mixing because, after quenching to −150 °C, excellent reproducibility was found in repeated DSC scans.

A TA Instruments (DSC 2910) differential scanning calorimeter calibrated with high-purity standards (*n*-heptane, *n*-octane, benzene, lauric acid, and indium) was used. DSC measurements were carried out in the temperature range from −150 to +215 °C (scanning rate 20 °C/min). The glass transition temperature T_g, cold crystallization temperature T_{cc}, and melting temperature T_m were evaluated from the DSC curves of melt-quenched samples. Two values were obtained for the melting temperature corresponding (a) to the peak of the melting endotherm ($T_m{}^p$) and (b) to the end of the melting process ($T_m{}^e$),[12] i.e., to the intercept between the baseline in the melt state and the steepest tangent to the high-temperature side of the melting endotherm. Both $T_m{}^p$ and $T_m{}^e$ were employed to analyze the melting point depression of PHB crystals induced by DBP. Diluent volume fraction Φ_1 was calculated from the reported density of amorphous PHB (1.177 g/cm³)[13] and of DBP (1.046 g/cm³)[14] at 20 °C, assuming volume additivity. An alternative calculation of Φ_1 at the melting temperature of the various mixtures was also carried out, using for the expansion coefficients of PHB[15] and DBP[14] the values 6×10^{-4} and 8.3×10^{-4}, respectively.

The growth of PHB spherulites in pure and plasticized PHB was observed with a Zeiss Axioscop polarizing optical microscope equipped with a Linkam TH 600 hot stage. Samples were

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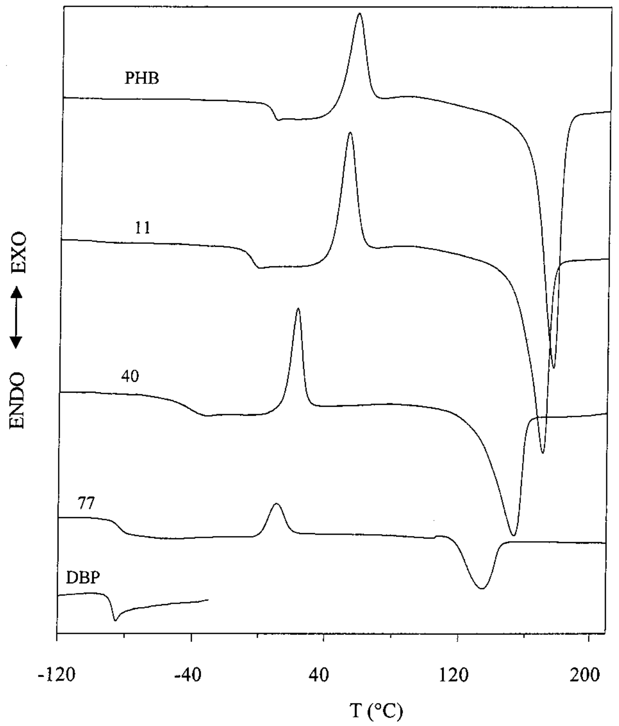

Figure 1. DSC curves of melt quenched PHB–DBP mixtures (DBP weight percent indicated on curves).

sandwiched between two microscope cover-glasses and heated at 20 °C/min to the melting temperature, where a gentle pressure on the upper glass produced a thin film. The samples were further heated at 10 °C/min up to 20 °C above T_m. Rapid cooling from the melt to the desired crystallization temperature T_c was obtained by means of N_2 gas flow (cooling rate higher than 250 °C/min). Isothermal crystallization studies were conducted at $T_c \leq 130$ °C to avoid PHB thermal degradation and loss of plasticizer during measurements. A new sample was used for each experiment. With the aid of an interfaced videocamera, real-time spherulite growth measurements were performed. Excellent reproducibility of growth rate results was obtained in repeated measurements on different spherulites.

Results and Discussion

Melting Behavior of Plasticized PHB. Figure 1 shows selected DSC curves of melt-quenched PHB–DBP mixtures that are representative of the thermal behavior of all polymer–diluent blends investigated. Apart from DBP, which only shows a glass transition at −91 °C, all DSC curves in Figure 1 display the glass transition, a cold crystallization exotherm with a main peak followed by a broad tail, and a single sharp melting endotherm. The temperature range of the three transitions systematically shifts to lower values with increasing DBP content, in line with the behavior expected for a polymer–diluent pair miscible at molecular level. In each mixture, the magnitude of the crystallization and melting phenomena is comparable, suggesting that quenching prevents PHB crystallization and yields a glassy amorphous PHB–DBP phase at low temperature. The curves of Figure 1 also show that with decreasing polymer content the intensity of crystallization and melting decreases. The enthalpy associated with the two processes gives evidence that PHB crystallizes to the same extent in the blends and in the pure state.[1]

The T_g–composition dependence of PHB–DBP mixtures has been reported and discussed in an earlier paper.[1] Figure 2 shows the crystallization (T_{cc}) and melting temperatures (T_m^p and T_m^e) of PHB–DBP blends as a function of composition. The temperature decrease of both phenomena is quite impressive and follows a very regular trend.

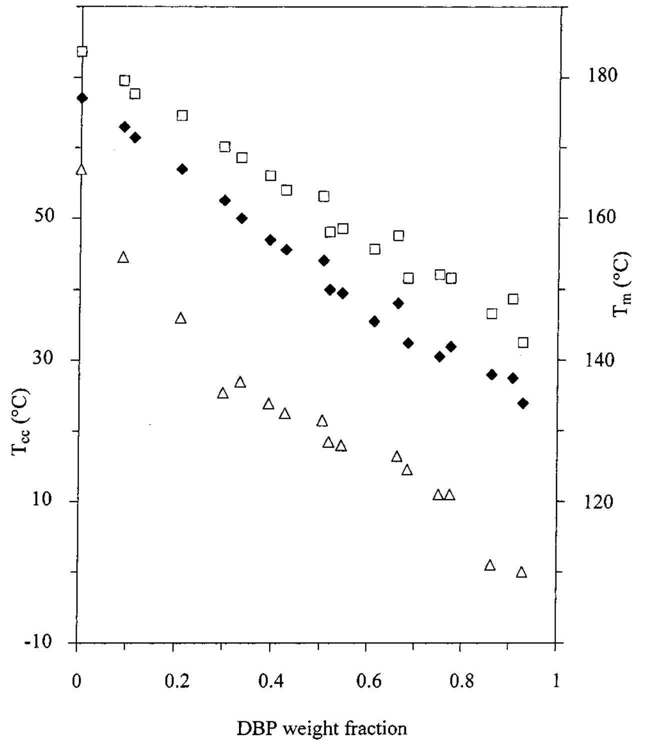

Figure 2. Composition dependence of cold crystallization temperature (T_{cc}, Δ) and melting temperatures (T_m^p, ◆; T_m^e, □) in PHB–DBP mixtures.

The melting point depression of a crystallizable polymer in a polymer–diluent mixture is usually described by the well-known expression developed by Flory and Huggins:[10]

$$1/T_m - 1/T_m^\circ = (R/\Delta H_u)(V_u/V_1)(\Phi_1 - \chi\Phi_1^2) \quad (1)$$

where subscripts 1 and u refer to the diluent and to the polymer segment, respectively. T_m° and T_m are the equilibrium melting points of the polymer respectively in the pure state and in the mixture with diluent volume fraction Φ_1, χ is the Flory–Huggins interaction parameter, R is the gas constant, V is the molar volume, and ΔH_u is the molar heat of fusion.

In the present work eq 1 was applied using Φ_1, V_u, and V_1 values calculated both at 20 °C and at the melting temperature of the mixtures investigated, obtaining identical results.

Application of eq 1 requires knowledge of the equilibrium melting points of the pure polymer and of the mixtures. The equilibrium melting point is usually obtained from isothermal crystallization experiments at different T_c's through extrapolation of T_m vs T_c, i.e., by means of the well-known Hoffman–Weeks plots.[16] However, this procedure cannot be applied to the system under investigation, because the high susceptibility of PHB to degradation at high temperature[17] prevents isothermal crystallization measurements near the melting temperature. A further problem arises from the impossibility to avoid volatilization of DBP during long crystallization experiments at high T_c's.

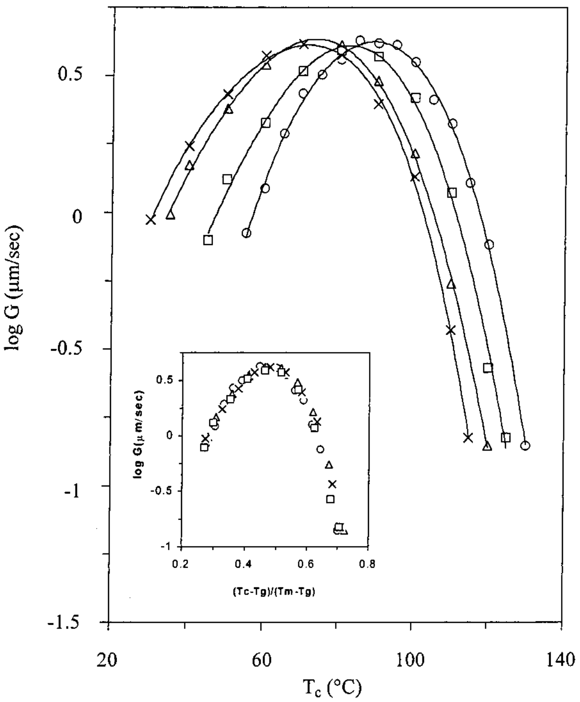

Figure 3. Radial growth rate G as a function of crystallization temperature T_c for PHB (○) and PHB−DBP mixtures with different DBP volume fractions (□, 0.1; △, 0.23; ×, 0.27). Inset: G vs reduced temperature $X = (T_c - T_g)/(T_m - T_g)$.

Although the DSC method employed for determining the melting points of PHB−DBP mixtures does not yield true thermodynamic transition temperatures, the results reported in Figure 2 clearly outline the basic properties of the binary system under investigation. The data in Figure 2 were therefore used in this paper to analyze the melting point depression according to eq 1. Both T_m^p and T_m^e were plotted as $[(1/T_m - 1/T_m^\circ)]/\Phi_1$ vs Φ_1, obtaining two straight lines as predicted by eq 1. Least-squares analysis of the data allowed determination of the interaction parameter χ (from the slope) and of ΔH_u (from the intercept). In both cases, i.e., by using T_m^p or T_m^e, very similar values of χ and ΔH_u were obtained. The interaction parameter is found to be small and negative (−0.1), indicating that PHB and DBP are thermodynamically miscible in the melt. The melting enthalpy of fully crystalline PHB derived from application of eq 1 to the experimental DSC results ($\Delta H_u = 11$ kJ/mol) very closely agrees with—and hence confirms—earlier literature data obtained from different experimental techniques.[13,18−20]

Kinetics of Spherulite Growth. Isothermal crystallization experiments were performed in the temperature range from 30 to 130 °C on PHB containing 0, 0.1, 0.23, and 0.27 DBP volume fraction. Volume-filling spherulites were observed in all cases, and the spherulite radius R grew linearly with time at all compositions and temperatures investigated. A constant value of the growth rate G (= dR/dt) implies constancy of composition of the molten phase from which the PHB crystals grow. During spherulite growth the noncrystallizable DBP diluent remains trapped in the interlamellar space, because its diffusion rate is slower than the spherulite growth rate. In the optical microscope the spherulites are seen to impinge along very neat lines, confirming that there is no DBP segregation at the growing front.

The radial growth rate G is plotted as a function of T_c in Figure 3 for the mixtures investigated. The curves show a maximum that shifts to lower temperature with increasing diluent content. Also, the shape of the curves slightly changes, with a modest but progressive broadening at the low-temperature branch. It is well-known that the crystallizability of a polymer is limited at low and high temperature by T_g and T_m, respectively. The shift of the crystallization curves of plasticized PHB to lower temperatures observed in Figure 3 is a direct consequence of the concomitant decrease of T_g and T_m with increasing diluent content (Figure 1). Since the decrease of T_g is more marked than that of T_m, this explains the broadening of the G vs T_c curves on the low-temperature side. The inset in Figure 3 shows that when the T_c values are normalized to take into account T_g and T_m changes and a reduced temperature scale $X = (T_c - T_g)/(T_m - T_c)$ is used, all G values fall onto a single crystallization "master curve" (with a maximum occurring at $X = 0.47$).

Figure 3 shows that the maximum growth rate G_{max} (ca. 5 μm/s) is not appreciably affected by the presence of DBP in the range of diluent contents investigated. This observation can be explained by the occurrence of a rather fortuitous counterbalance of the following opposite effects of diluent addition on the crystallization rate of PHB: on one hand, the growth rate should increase due to T_g depression that enhances chain mobility; on the other hand, the growth rate should decrease owing to the "dilution effect", i.e., to the reduction of the number of crystallizable polymer segments available at the lamellae growing front. Apparently, neither of the two effects predominates in the composition range investigated, leaving the G_{max} value practically unaltered.

The temperature dependence of the spherulite growth rate G for homopolymers, according to the Lauritzen−Hoffman treatment,[9] is given by

$$G = G_0 \exp(-U^*/R(T_c - T_\infty)) \exp(-K_g/fT_c\Delta T) \quad (2)$$

where the preexponential factor G_0 is essentially temperature-independent and usually considered as a constant, U^* is the activation energy for transport of crystallizable segments to the crystal front through the undercooled melt, T_∞ is the temperature below which segmental motions cease, $\Delta T = T_m^\circ - T_c$ is the degree of undercooling, T_m° is the equilibrium melting point, and $f = 2T_c/(T_m^\circ + T_c)$ is a correction factor accounting for the temperature dependence of the melting enthalpy. All temperatures must be expressed in kelvin. The nucleation constant K_g is given by

$$K_g = \frac{n b_0 \sigma \sigma_e T_m^\circ}{k \Delta H_m} \quad (3)$$

where b_0 is the thickness of a molecular layer, σ and σ_e are the lateral and fold surface free energies of the growing crystal, respectively, ΔH_m is the melting enthalpy per unit volume, and k is the Boltzmann constant. The value of the parameter n is characteristic of the crystallization regime and changes from $n = 4$ (regime I, low undercoolings) to $n = 2$ (regime II, intermediate undercoolings) and back to $n = 4$ for high undercoolings (regime III).

To analyze the growth kinetics of PHB spherulites in the framework of Lauritzen−Hoffman theory, the quantity $\ln G + U^*/R(T_c - T_\infty)$ was plotted as a function of $1/fT_c\Delta T$, taking $U^* = 10\ 250$ J/mol;[13] values of T_∞ and

Table 1. Parameters Derived from Analysis of Growth Rate Data for PHB−DBP Mixtures

DBP ϕ_1	T_∞ (K)	$T_m°$ (K)	$G_0 \times 10^{-11}$ (μm/s)	$K_g \times 10^{-5}$ (deg^2)	$\sigma\sigma_e \times 10^{12}$ (J^2/cm^4)	$K_g/T_m° \times 10^{-3}$	R^2
0	229	473	2.97	5.48	12.8	1.160	0.9986
0.1	220	469	3.04	5.45	12.9	1.162	0.9961
0.23	205	465	3.07	5.41	12.9	1.163	0.9980
0.27	200	462	3.25	5.37	12.9	1.162	0.9972

of $T_m°$ were obtained by trial and error, as temperatures which gave the best correlation coefficient in fitting the experimental G data. The least-squares method yields $T_m° = 473$ K and $T_\infty = 229$ K, the former corresponding to the experimental $T_m^e + 16.5$ K and the latter to $T_g - 50$ K. Both values are in very good agreement with earlier data reported in the literature[13,21] for PHB. In addition, all data (covering a crystallization temperature range from 55 to 130 °C) fall on a single line, i.e., show no regime transitions. In line with the results of Barham[13] and of Pearce et al.,[21] who identified a transition from regime II to regime III around 130−140 °C, the present data are attributed to regime III crystallization.

Turning now to the analysis of PHB spherulite growth in the presence of DBP, additional terms must be considered to account for the presence of the diluent,[22,23] and eq 2 must be consequentially modified. The equation proposed by Boon and Azcue[3] to describe the growth rate of spherulites of a crystallizable polymer in a single-phase melt containing a low molecular weight diluent has the following form:

$$G = \phi_2 G_0 \exp(-U^*/R(T_c - T_\infty)) \exp[(-K_g/fT_c\Delta T) + (2\sigma T_m° \ln \phi_2/fb_0\Delta H_m\Delta T)] \quad (4)$$

where ϕ_2 is the volume fraction of crystallizable polymer and the values of T_∞ and $T_m°$ are composition-dependent. The preexponential factor G_0 is multiplied by ϕ_2 to account for the dilution due to the low molecular weight component; the additional term in the second exponential is an entropic contribution to the free energy of activation for nucleus formation, which accounts for the probability of selecting the required number of crystallizable polymer sequences from the mixture at the given ϕ_2 concentration.

It is convenient to rearrange eq 4 in the form

$$\ln G + U^*/R(T_c - T_\infty) - \ln \phi_2(1 + 2\sigma T_m°/fb_0\Delta H_m\Delta T) = \ln G_0 - K_g/fT_c\Delta T \quad (5)$$

which predicts a linear dependence of the left-hand side of the equation (hereafter indicated as *alfa*) on $1/fT_c\Delta T$. The slope and intercept of the line yield K_g and G_0, respectively.

For each PHB−DBP mixture investigated *alfa* was plotted against $1/fT_c\Delta T$. The lateral surface free energy σ was obtained by using the Hoffman modification[24] of the Thomas−Staveley relation:[25]

$$\sigma = \alpha_{LH}(\Delta H_m)(a_0 b_0)^{1/2} \quad (6)$$

where the value of the α_{LH} constant quoted for high-melting polyesters is 0.23[26] and the cross-sectional area of a chain in the crystal $(a_0b_0)^{1/2}$ is equal to 6.17 Å for PHB.[27] The literature value for plain PHB[13] was used for the activation energy U^* (10 250 J/mol), whereas $T_m°$ and T_∞ were allowed to vary in order to maximize the correlation coefficient of the linear fit to the plotted data. The obtained $T_m°$ and T_∞ values for the PHB−DBP mixtures investigated are collected in Table 1. It is interesting to note that these values parallel the changes with composition of the experimental melting and glass transition temperatures, the differences $T_m° - T_m^e$ and $T_g - T_\infty$ remaining practically constant and equal to 17.5 ± 1 and 49 ± 1 K, respectively.

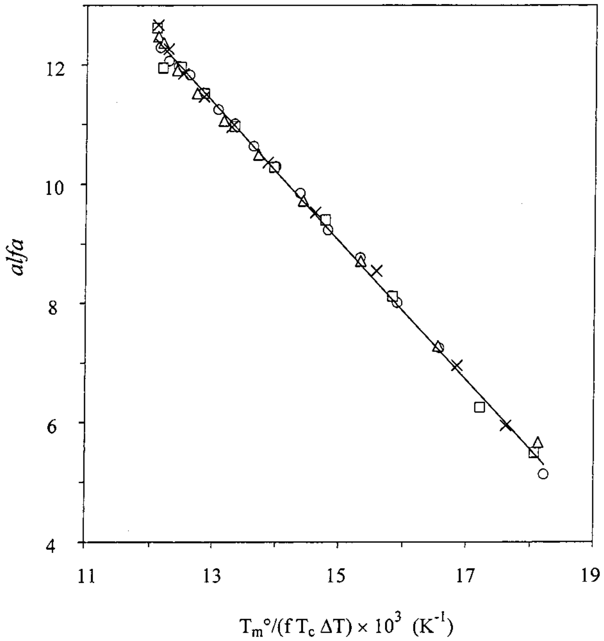

Figure 4. Plot of *alfa* (see eq 5) against $T_m°/(fT_c\Delta T)$ for PHB (○) and PHB−DBP mixtures with different DBP volume fractions (□, 0.1; △, 0.23; ×, 0.27).

The values of K_g, obtained from the slope of the linear fits to the data plotted according to eq 5, are listed in Table 1. K_g is seen to decrease slightly with increasing DBP content, a behavior that reflects the depression of $T_m°$ induced by the diluent (see eq 3).

Figure 4 shows that when *alfa* of eq 5 is plotted as a function of $T_m°/fT_c\Delta T$, using the best-fit data of $T_m°$ and T_∞ reported in Table 1, all growth rate results collected in the present investigation fall on the same straight line. The slope of the line corresponds to $K_g/T_m°$. By substituting the value of $K_g/T_m°$ in eq 3, the product of the surface free energies $\sigma\sigma_e$ (12.9 × 10^{-12} J^2/cm^4) is obtained, which closely agrees with earlier estimates.[13,21,28] Over the limited composition range examined $\sigma\sigma_e$ is seen to be independent of DBP concentration. This observation suggests that, in addition to widening the crystallization window by increasing the $T_m - T_g$ interval, the presence of DBP does not appreciably alter the mechanism of PHB spherulite formation. The work required to make a fold ($q = 2a_0b_0\sigma_e$) remains the same also in the polymer−diluent mixtures, an observation already reported for other binary systems.[29−31]

Conclusions

The DBP diluent is miscible at molecular level with the natural polyester PHB. In PHB/DBP mixtures both the glass transition and melting temperatures decrease with increasing diluent content, the shift of T_g being more pronounced than that of T_m. The whole crystallization window moves to lower temperatures and broadens, as reflected by the changes of the cold crystallization process in dynamic DSC scans and by the shifts of the isothermal spherulite growth rate curves. It is interesting to note that the maximum growth rate (G_{max}) does not change in the range of diluent contents explored and that all isothermal crystallization data fall on the same master curve when the crystallization temperatures are normalized to account for the T_g and T_m changes with composition. The constancy of G_{max} indicates that in the polymer–diluent mixtures investigated the opposite “dilution” and “chain mobility” effects—which should respectively decrease and increase the crystal growth rate—tend to compensate.

The value of the melting enthalpy of fully crystalline PHB obtained in this work from the analysis of the melting point depression shows excellent agreement with earlier data from other sources, as does the estimate of the product of the crystal surface free energies $\sigma\sigma_e$ obtained from the isothermal crystallization results of this study. Noteworthy, in the PHB/DBP system, the $\sigma\sigma_e$ value does not change with composition in the range of DBP contents investigated.

Finally, the equilibrium $T_m°$ and T_∞ values derived in this work from the analysis of the isothermal crystallization results very closely follow the experimental T_m and T_g changes with diluent content obtained from dynamic DSC measurements.

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