Crystallization kinetics in blends of isotactic and atactic poly(β-hydroxybutyrate)

R. Pearce, G. R. Brown and R. H. Marchessault*
Department of Chemistry, McGill University, Montreal, Quebec, Canada, H3A 2A7
(Received 2 July 1993; revised 4 February 1994)

Isothermal crystallization kinetics in the miscible blend system isotactic/atactic poly(β-hydroxybutyrate) (PHB) are examined by optical microscopy. The presence of the atactic component results in a reduction in spherulitic growth rate of the isotactic polymer. Analysis of the growth rates using the Lauritzen–Hoffman model shows that a regime II→III transition is present for all blend compositions investigated (0–50 wt% atactic), and that this transition occurs at a constant temperature of 140°C. The ratio of the nucleation constants for the two regimes, K_g^{III}/K_g^{II}, is found to deviate from the theoretical value of 2.0 in the blend system. It is shown that a modified version of the Lauritzen–Hoffman equation incorporating entropic effects is unable to account for these deviations. The work of chain-folding, q, is calculated to be 5.1 kcal mol^{-1} for isotactic PHB. The implications of using assumed values of the transport parameters in the kinetic analysis are discussed.

(Keywords: poly(β-hydroxybutyrate); blends; crystallization kinetics)

INTRODUCTION

There are numerous reports in the literature of studies of crystallization kinetics in homopolymers as determined from measurements of spherulitic growth rates[1–11]. The theoretical framework for such studies was originally developed by Turnbull and Fisher in 1949[12], and subsequently reformulated in molecular terms by Hoffman and co-workers[3,13–21]. The latter treatment, usually referred to as the Lauritzen–Hoffman theory, expresses the linear growth rate G as follows[16]:

$$G = G_0 \exp\left(\frac{-U^*}{R(T-T_\infty)}\right)\exp\left(\frac{-K_g}{fT\Delta T}\right) \tag{1}$$

where the pre-exponential factor G_0 contains terms which are essentially temperature-independent, U^* is the activation energy for transport of crystallizable segments to the crystallization front, T_∞ is the temperature below which such motions cease, T is the crystallization temperature, $\Delta T = T_m^0 - T$ is the degree of undercooling, T_m^0 is the equilibrium melting point, f is a factor which accounts for the variation in the enthalpy of fusion Δh_f with temperature and is given by $f = 2T/(T_m^0 + T)$. The nucleation constant K_g can be expressed as[16,18]:

$$K_g = \frac{n b_0 \sigma \sigma_e T_m^0}{\Delta h_f k} \tag{2}$$

where σ and σ_e are the lateral and end-surface free energies, respectively, of the growing crystal, b_0 is the molecular thickness and k is the Boltzmann constant. The value of n depends on the regime of crystallization. At high temperatures (low undercoolings) each surface nucleation occurrence leads to rapid completion of the growth strip prior to the next nucleation event[16]. This is referred to as regime I and $n = 4$. At lower temperatures, in regime II, multiple surface nuclei form on the substrate and $n = 2$. When crystallization occurs at still lower temperatures, the separation between the multiple nuclei characteristic of regime II reaches its minimum value. This is regime III and $n = 4$. Regime transitions are observed experimentally as abrupt changes of slope in plots of $\ln G + U^*/R(T - T_\infty)$ as a function of $1/(fT\Delta T)$, as seen schematically in *Figure 1*[16]. The ratios of the slopes K_g^{III}/K_g^{II} and K_g^{I}/K_g^{II} are predicted to be 2. Such transitions have been observed for a number of polymers[22], although very few have shown evidence of all three regimes.

Spherulitic growth kinetics in miscible blends of non-crystalline/crystalline polymers have also been reported in the past[1,23–40]. With one exception[32], all of the previous reports have indicated a depression in growth kinetics of the crystallizable component upon addition of the non-crystallizable component. This depression in kinetics has been attributed to such factors as a reduction in chain mobility due to an increase of the glass transition temperature T_g, dilution of the crystallizable component at the growth front, changes in free energy of nucleation due to specific interactions and competition between the advancing spherulitic front and diffusion of the non-crystallizable component into interlamellar and interfibrillar regions. Interestingly, there has been only one systematic study of regime transitions in blends[40].

In this study, the spherulitic growth rates of bacterial poly(β-hydroxybutyrate) (PHB) in its blends with synthetic, atactic PHB are reported. The bacterial version of PHB is highly crystalline[11,41] and isotactic in its chain configuration. This blend system is especially attractive for a kinetic study since growth rates can be obtained over an exceptionally wide temperature range (from 150 to 40°C). Furthermore, since most crystalline polymers contain small amounts of low molecular weight and/or

---

*To whom correspondence should be addressed

0032-3861/94/18/3984–06

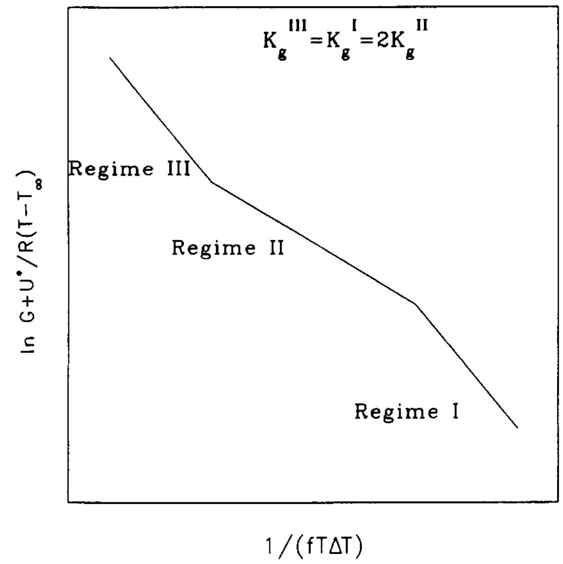

Figure 1 Schematic representation of regime transitions as predicted by the Lauritzen–Hoffman model of crystallization kinetics

atactic material as impurities, this system is more like those used industrially than those examined in many previous kinetic studies, which have tended to consider only narrow molecular weight fractions. In a preliminary study we reported on the melting behaviour of solvent-cast films of this blend[42], and another study has appeared demonstrating a depression of the melting point in this system[43].

A previous study has shown bacterial PHB to exhibit a regime II→III transition[11]. In this report, the kinetics of crystallization will be analysed using the Lauritzen–Hoffman model, and it will be demonstrated that a regime II→III transition also occurs in blends of isotactic and atactic PHB. It is shown that the ratio of the nucleation constants K_g^{III}/K_g^{II} deviates from the predicted value of 2 and that this deviation cannot be accounted for by invoking entropic effects[23]. In addition, results will be presented on the depression of the equilibrium melting point T_m^0 of bacterial PHB in its blends with atactic PHB, obtained by the Hoffman–Weeks technique[44]. Finally, the implications of making assumptions about the parameters present in the Lauritzen–Hoffman equation are discussed.

EXPERIMENTAL

Bacterial PHB was obtained from Marlborough Biopolymers (Billingham, UK). It was purified by dissolution into *N*,*N*-dimethylformamide (DMF) and reprecipitation into a large excess of stirred diethyl ether. Synthetic, atactic PHB was supplied by Polysar Rubber Corporation (Sarnia, Ontario, Canada) and was prepared from racemic β-butyrolactone using a catalyst[45,46] prepared from $ZnEt_2/H_2O$. It was purified by dissolution in chloroform and reprecipitation into diethyl ether.

Molecular weight characterization of the samples was performed by gel permeation chromatography (g.p.c.) in chloroform, using standard polystyrene samples for calibration. The results are presented in *Table 1*, together with the thermal transitions of the two component polymers. The tacticities of these polymers, as determined by solution ^{13}C n.m.r., have been reported previously[42].

Blends of isotactic and atactic PHB for differential scanning calorimetry (d.s.c.) were prepared from 1% solutions of each in chloroform. The resultant solutions were filtered onto Teflon and the solvent was allowed to evaporate overnight. The films were then dried for 24 h under vacuum at room temperature.

D.s.c. measurements were performed with a Perkin-Elmer DSC7 equipped with an intracooler system. Isothermal crystallization experiments were conducted with approximately 0.5 mg samples sealed in aluminium pans. These were heated at 20°C min^{-1} under a nitrogen atmosphere to a temperature 15°C above the melting peak temperature, held there for 1 min, and quenched at a nominal rate of 200°C min^{-1} to a preselected crystallization temperature, where they were held isothermally for 1 h. The samples were then heated at 20°C min^{-1} to 190°C and the melting point was recorded at the peak temperature. A new sample was used for each run and indium was used for calibration.

Samples for optical microscopy were prepared by filtering stirred chloroform solutions of the two components onto cleaned glass cover-slips. The solvent was then evaporated as described above. The resultant films were typically 5–10 μm thick. A new sample was used for each crystallization experiment.

Measurements of the spherulitic growth rates by optical microscopy were performed using a Nikon Optiphot polarizing microscope equipped with a Linkam THMS 600 hot stage. Samples were heated on the hot stage at 20°C min^{-1} to a temperature 15°C above the d.s.c. melting peak temperature. After holding at this temperature for 1 min, the samples were quenched at 130°C min^{-1} to an isothermal crystallization temperature. Spherulitic growth was monitored under crossed polars using a video camera mounted on the microscope. The images were recorded on video tape and the JAVA (Jandel Scientific) image analysis software was used to determine spherulite size at various crystallization times. In a typical experiment, 20 to 30 readings were made for each spherulite and the change in size was ca. 100 μm. Linear growth rates were obtained with correlation coefficients of 0.999 or better by plotting diameter as a function of time.

RESULTS AND DISCUSSION

Equilibrium melting points

From Hoffman and Weeks[44] the relation between the observed melting point T_m and the isothermal crystallization temperature T_c is given by:

$$T_m = T_m^0\left(1-\frac{1}{\gamma}\right)+\frac{T_c}{\gamma} \qquad (3)$$

where γ is the ratio of the initial to the final lamellar thicknesses and T_m^0 is the equilibrium melting point, obtained from a plot of T_m as a function of T_c by extrapolating the linear data until intersection with the $T_m = T_c$ line. The data obtained for the isotactic/atactic PHB blend system are plotted in *Figure 2* and the results

Table 1 Characteristics of PHB samples

PHB sample	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	T_m(°C)	T_g(°C)
Bacterial PHB	445	137	3.2	177	4
Atactic PHB	21	11	1.9	n.a.	4

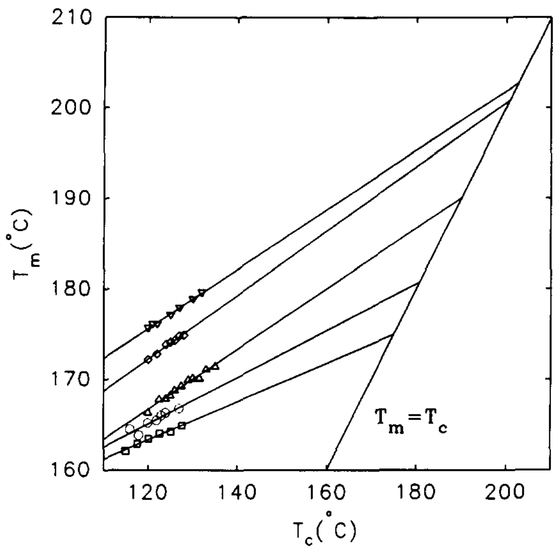

Figure 2 Hoffman–Weeks plots for the blend system isotactic/atactic PHB: ▽, 100% isotactic PHB; ◇, 90/10 isotactic/atactic; △, 75/25 isotactic/atactic; ○, 60/40 isotactic/atactic; □, 50/50 isotactic/atactic

Table 2 Equilibrium melting points T_m^0 for isotactic/atactic PHB blends

Atactic PHB (wt%)	T_m^0(°C)
0	203 ± 3
10	201 ± 3
25	190 ± 3
40	183 ± 4
50	175 ± 3

are summarized in *Table 2*. Each point is an average from at least two runs. The variation in slopes is of similar magnitude to that seen in other blend systems[27,31,44] and arises from a variation in γ. The depressions reported here are significantly different from those reported previously[43] and reflect the fact that the measurements in this study involve smaller undercoolings[47]. Nonetheless, the range of approximately 30–70°C over which extrapolations are carried out in the present work is still substantial. The value of $T_m^0 = 203 \pm 3$°C obtained for 100% isotactic PHB agrees well with other estimates in the literature. For example, Marchessault *et al.*[41] found $T_m^0 \approx 200$°C and Barham *et al.*[11] found $T_m^0 = 200 \pm 5$°C. Shorter extrapolations were used for the blends; however, the uncertainties in T_m^0 are of similar magnitude as those for 100% isotactic PHB.

Spherulitic growth kinetics

Volume-filling spherulites of isotactic PHB were obtained at all compositions investigated (0–50% atactic PHB). Furthermore, all growth rates were linear with time, in some cases for 1 h or more, and no phase separation could be detected. Hence, it can be concluded that there is no rejection of atactic PHB into interspherulitic regions[1].

Figure 3 shows the variations of linear growth rates with crystallization temperature T_c for pure isotactic PHB and its blends with atactic PHB. A pronounced retardation in the rate of crystallization occurs upon addition of the second component. For example, the maximum growth rate, G_{max}, for the 50/50 blend is approximately one quarter of that for 100% isotactic PHB. There is also a gradual shift in G_{max} towards higher crystallization temperatures as atactic PHB is added. This shift in peak maximum has been observed also in other blend systems[24,25] and most notably in the work of Keith and Padden[1] on blends of atactic and isotactic polymers. It is significant that this shift in G_{max} is opposite to that expected from changes in the melting point, nor can changes in T_g be invoked since it is invariant for this blend system.

The Lauritzen–Hoffman model, as described by equation (1), was used to analyse the data according to the usual procedure[16]. The quantity $\ln G + U^*/R(T - T_\infty)$ was plotted against $1/(fT\Delta T)$, while varying U^* and T_∞ to maximize the correlation coefficient. It was not possible to fit all the data, from $T = 150$ to 40°C, on one straight line. Instead, as seen in *Figure 4*, a discontinuous change in slope was observed at a crystallization temperature of 140°C, corresponding to an undercooling of $\Delta T = 63°C$ for pure isotactic PHB. This is indicative

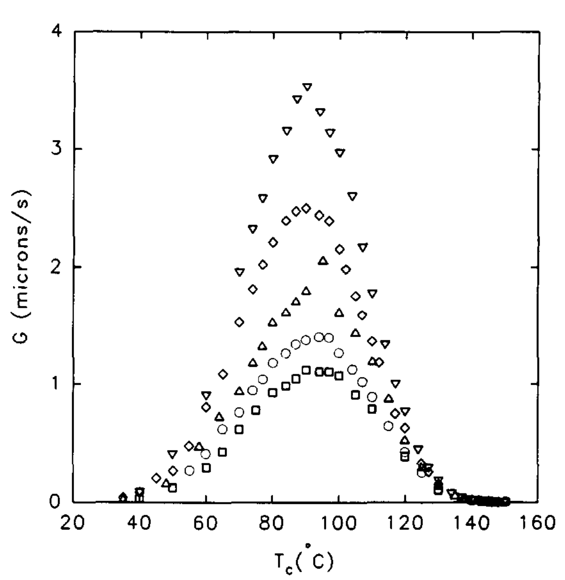

Figure 3 Spherulitic growth rates in the blend system isotactic/atactic PHB: ▽, 100% isotactic PHB; ◇, 90/10 isotactic/atactic; △, 75/25 isotactic/atactic; ○, 60/40 isotactic/atactic; □, 50/50 isotactic/atactic

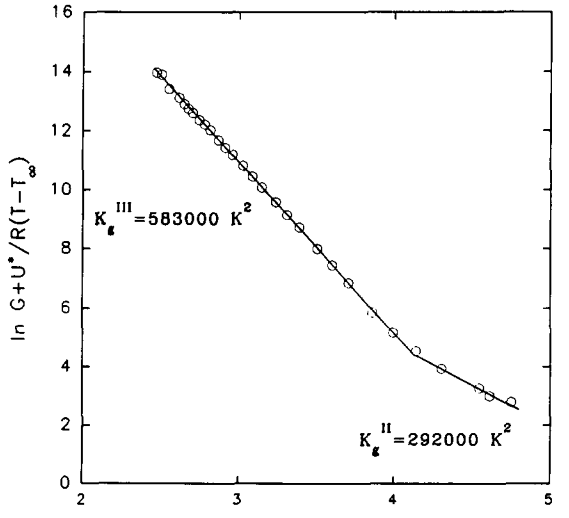

Figure 4 Plot of $\ln G + U^*/R(T - T_\infty)$ *versus* $1/(fT\Delta T)$ for 100% isotactic PHB

Table 3 Parameters from Lauritzen–Hoffman model for isotactic/atactic PHB blends

Atactic PHB (wt%)	U^* (kcal mol^{-1})	T_∞ (K)	K_g^{III} (K^2) $\times 10^{-5}$	K_g^{II} (K^2) $\times 10^{-5}$	K_g^{III}/K_g^{II}	G_0^{III} (cm s^{-1})	G_0^{II} (cm s^{-1})
0	2.75	226	5.83	2.92	2.0	1.2×10^8	7.5×10^6
10	2.61	224	5.17	2.60	2.0	9.0×10^5	1.5×10^2
25	2.70	223	3.60	1.47	2.4	2.5×10^5	4.7
40	2.49	222	2.67	0.98	2.7	7.5×10^3	0.4
50	2.31	226	1.95	0.59	3.3	6.0×10^2	0.1

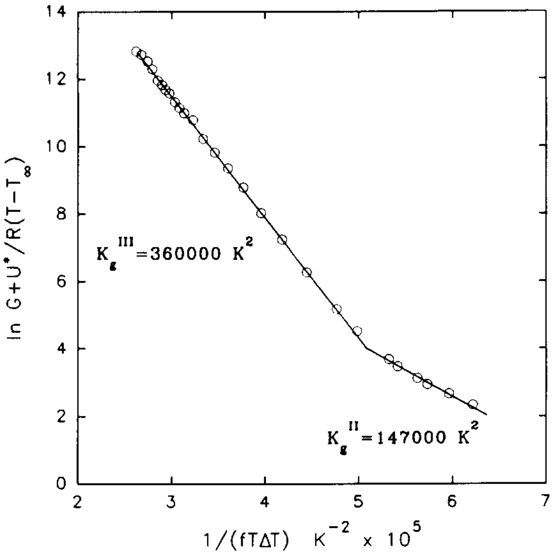

Figure 5 Plot of $\ln G+U^*/R(T-T_\infty)$ *versus* $1/(fT\Delta T)$ for the blend 75/25 isotactic/atactic PHB

of a regime II→III transition that has been reported previously for isotactic PHB[11]. An optimum fit was obtained using $U^*=2750$ cal mol^{-1} and $T_\infty=226$ K, the latter corresponding to T_g-47 K. The ratio of the slopes of the two linear portions is 2.0, in agreement with the predicted value[18] of K_g^{III}/K_g^{II}. The values obtained for U^* and T_∞ also agree well with those of a previous study of isotactic PHB crystallization[11].

Equation (1) was used without modification to analyse the growth kinetics for the blends as well. A typical fit is shown in *Figure 5* for a blend of 75% isotactic/25% atactic PHB. The discontinuity attributed to the regime II→III transition is still apparent at 140°C. For this blend the best-fit values of the parameters U^* and T_∞ were found to be 2700 cal mol^{-1} and 223 K, respectively. Quite significantly, however, the ratio of the two slopes, K_g^{III}/K_g^{II}, increased to 2.4 from the predicted value of 2.0. As shown in *Table 3*, this ratio continues to increase as the fraction of atactic component in the blend is increased. Correlation coefficients were always superior to 0.999 for the low-temperature regime III data and approximately 0.99 for the high-temperature regime II data.

To demonstrate that the deviation of the slope ratios from the predicted value is not a result of experimental error in the equilibrium melting points, the analysis was repeated with various values of T_m^0. In the case of the 25% atactic PHB blend, a slope ratio of 2 could only be obtained using a value of 208°C for T_m^0. This is clearly unrealistic since it is 5°C higher than the equilibrium melting point of the pure isotactic component. It is also interesting that the position of the regime II→III transition remained at 140°C regardless of the composition of the blend or the value of T_m^0 used.

Table 4 Calculated values of K_g^{III} and correlation coefficients for 100% isotactic PHB using different values of transport parameters

U^* (kcal mol^{-1})	T_∞ (K)	K_g^{III} (K^2) $\times 10^{-5}$	Correlation coefficient
1.50	T_g-30	4.60	0.9934
4.12	$T_g-51.6$	7.99	0.9889
2.75	T_g-47	5.83	0.9997

It is important to note that in our analysis of crystallization kinetics the parameters U^* and T_∞ were treated as variables in order to maximize the quality of the fit to equations (1) and (4). In many cases in the literature these parameters have simply been assigned the values $U^*=1500$ cal mol^{-1} and $T_\infty=T_g-30$ K, as appropriate to many polymers, or the Williams–Landel–Ferry (WLF)[48] values $U^*=4120$ cal mol^{-1} and $T_\infty=T_g-51.6$ K. It is frequently necessary to make such assumptions, especially in cases where it is difficult or impossible to obtain data at high undercoolings, where the kinetics are controlled by the rate of segment transport. However, in the case of isotactic PHB both parameter assignments gave values of the nucleation constant K_g that differed greatly from the best-fit value. This is illustrated in *Table 4* for the regime III data. The results for the high-temperature regime II data are essentially independent of parameter choice. It is apparent that while both of the parameter assignments mentioned above give reasonable correlation coefficients, the values of K_g can be in error by as much as 40% when compared to the best-fit result.

The analysis of spherulitic growth rates in polymer blends by use of equation (1) can be questioned, of course, since this equation has no terms to account for the presence of a non-crystallizable component. Several studies[24,27,31,36–40] of crystallization kinetics in blends have made use of a modified version of equation (1) due to Boon and Azcue[23]:

$$G=\phi_2 G_0 \exp\left(\frac{-U^*}{R(T-T_\infty)}\right)\exp\left(\frac{-K_g}{fT\Delta T}+\frac{2\sigma T_m^0 \ln\phi_2}{fb_0\Delta h_f\Delta T}\right) \tag{4}$$

In this version of the kinetic equation, the pre-exponential factor is multiplied by ϕ_2, the volume fraction of the crystallizable component, to account for the dilution by the second component. The additional term in the second exponential, proportional to $\ln\phi_2$, arises from an entropic contribution to the free energy of activation for nucleus formation. We make use of the empirical relation[15]:

$$\sigma = \alpha(\Delta h_f)(a_0 b_0)^{1/2} \tag{5}$$

with $\alpha = 0.25$ as appropriate to high-melting polyesters[19]. Substitution of equation (5) into equation (4) and using literature[11] values of $a_0 = 6.6$ Å and $b_0 = 5.8$ Å results in:

$$\ln G + \frac{U^*}{R(T - T_\infty)} - \frac{0.534 T_m^0 \ln \phi_2}{\Delta T} = \ln(G_0 \phi_2) - \frac{K_g}{f T \Delta T} \tag{6}$$

When the left-hand side of equation (6) was plotted against $1/(fT\Delta T)$, using the same optimization procedure as described above, it was found that the optimum transport parameters U^* and T_∞ are unaffected by the additional term in the nucleation exponential. However, the difficulty encountered with the ratios of the slopes was actually worsened. For example, in the case of the 25% atactic PHB blend, use of equation (6) yielded $K_g^{III} = 325\,000\,\mathrm{K}^2$, $K_g^{II} = 114\,000\,\mathrm{K}^2$, with $K_g^{III}/K_g^{II} = 2.85$. This reflects the $1/\Delta T$ dependence in the additional term, which affects more the data at low undercooling. It is thus apparent that the deviation of the slope ratios away from the theoretical value is not due to entropic factors, at least not as represented by equation (4), and that this expression may not be appropriate in all blend cases. It should be noted, however, that this equation was originally derived for small molecule additives[23].

It is a simple matter to obtain σ and σ_e for isotactic PHB by the use of equation (2). Using the literature[11] value of $\Delta h_f = 1.85 \times 10^8\,\mathrm{J\,m^{-3}}$ and equation (5) with $\alpha = 0.25$ yields $\sigma = 29\,\mathrm{erg\,cm^{-2}}$ and $\sigma_e = 46\,\mathrm{erg\,cm^{-2}}$. The latter value agrees reasonably well with a previously reported value of $38 \pm 6\,\mathrm{erg\,cm^{-2}}$ determined by measurements of lamellar thickness[11]. There has appeared recently a report of $\sigma_e = 96\,\mathrm{erg\,cm^{-2}}$ in blends of isotactic PHB and poly(epichlorohydrin)[39]. However, this value was obtained using $\alpha = 0.1$ in equation (5), which is inappropriate for high-melting polyesters such as PHB. Furthermore, any estimate of σ_e obtained from an analysis of kinetics based on assumed values of the transport parameters should be viewed with caution given the errors in K_g that can result from such assumptions (see above).

It has been suggested[16] that the parameter most closely related to chain structure is q, the work of chain-folding, given by $q = 2a_0 b_0 \sigma_e$. Generally it has been observed that q is roughly proportional to chain stiffness[4,5,16,35]. Flexible chains such as polyethers, which exhibit free rotation about the C–O–C bonds, have q values[16] of ca. $3\,\mathrm{kcal\,mol^{-1}}$; polymers with moderately stiff chains without bulky side-groups, such as polyethylene, have $q \sim 5\,\mathrm{kcal\,mol^{-1}}$ and vinyl polymers with bulky side-groups, such as polystyrene, have q values of ca. $7\,\mathrm{kcal\,mol^{-1}}$ and above. For isotactic PHB the value $q = 5.1\,\mathrm{kcal\,mol^{-1}}$ is obtained. This value fits into the category of moderately stiff chains and is slightly above that of $4.7\,\mathrm{kcal\,mol^{-1}}$ for poly(L-lactic acid)[49], a polyester of structure very similar to that of PHB, but less than the value of $7.9\,\mathrm{kcal\,mol^{-1}}$ for poly(pivalolactone)[49], which has two methyl side-groups compared to one methyl for PHB and poly(L-lactic acid).

SUMMARY AND CONCLUSIONS

It is apparent from the results in *Table 3* that the retardation in spherulitic growth rates is reflected almost entirely in the pre-exponential factors G_0. While the kinetic equation including the entropic contributions to the free energy of nucleation, equation (4), suggests a simple linear dependence of the pre-exponential factor on volume fraction of the crystallizable component, it can be seen from the data in *Table 3* that the effect is actually more severe. In a treatment of crystallization kinetics that incorporates the effects of chain reptation, Hoffman[17,18,21] demonstrates that the effect of friction from steady-state reptation is reflected in the pre-exponential factor. When this effect is due to molecular weight M, it is found that G_0 varies as M^{-1}. Hence within this context our results suggest that dilution with a non-crystallizable component is analogous to an increase in molecular weight of the crystallizable component, since both result in an increase in the friction coefficient associated with reptation. Moreover, De Gennes has treated the case of a long chain dispersed in a melt of shorter chains of the same chemical composition[50]. He points out that the mobility of the long chain can actually be due to both reptation and hydrodynamic diffusion.

It is interesting that the gradual shift in the maximum growth rate towards increasing temperature upon addition of the second component (see above) is reflected in a lowering of the nucleation constants, the transport terms remaining essentially constant. The latter result is especially notable since it seems to reinforce the ideas put forth by Hoffman and co-workers[15,16] that the molecular motions reflected in U^* and T_∞ are not those associated with viscous flow and fluidity. Were this not so, a more dramatic decrease in U^* should occur upon dilution owing to a lowering of the viscosity that results from addition of the atactic polymer with much lower molecular weight.

The result that the regime II→III transition temperature remained constant with blend composition is most interesting and has not been seen previously in the literature. Furthermore, the position of this transition temperature was unaffected by the value of the melting point used in the analysis. There has been evidence to suggest that this is not the case for the regime I→II transition temperature, which appears to occur at a constant undercooling[3]. However, it has been suggested[6] that the position of a regime II→III transition should be determined by molecular dynamics as reflected by T_g and not by undercooling. The invariance of T_g with composition for the system examined here seems to reinforce this proposal. Although the regime transition is located in the high-temperature region, where the crystal growth is nucleation-controlled, it is reasonable that segmental motion as reflected by T_g has a role in the process of surface nucleation. Hoffman *et al.*[49] have indicated that surface nucleation involves, in part, the 'localization' of a section of a chain, previously part of a random coil liquid, prior to actual crystallographic attachment.

Our results show a regular increase in the slope ratios K_g^{III}/K_g^{II} from the theoretical value of 2 as atactic component is added. Such deviations have been seen in the past in the case of single-component homopolymer systems and have been associated with polydisperse samples[6,8]. In the one previous systematic study of regime transitions in blends[40], the authors reported a ratio K_g^{III}/K_g^{II} greater than 4 when U^* was allowed to vary so as to maximize the quality of the fit to equation (6), although T_∞ was fixed at the WLF value. There is also a report[28] of a slope ratio of approximately 4 for a regime II→III transition in the blend system isotactic polystyrene/poly(vinyl methyl ether).

It is difficult to explain the source of these deviations from the behaviour predicted by the Lauritzen–Hoffman model. The present study illustrates that either the nucleation term requires some modification or the end-surface free energy σ_e changes with regime, although there exist no theoretical grounds for the latter assertion. However, Point *et al.*[51] have suggested recently that the apparent presence of a regime II→III transition in poly(ethylene oxide) is actually a reflection of a change in the crystallographic orientation at the growth face. It remains to be determined whether this also applies to other instances of observed regime transitions.

Alfonso and Russell have put forth a phenomenological equation to account for crystallization kinetics in miscible blends[29], but this requires values for the self-diffusion coefficients which are not available in most cases. However, their approach does emphasize the important role played by the diffusion of the non-crystallizable component away from the growth front as well as the transport of the crystallizable component towards it. This is in accordance with the morphological studies of Keith and Padden[1], as well as our results, which suggest that the effect of the non-crystallizable component is not simply entropic in origin.

In this paper we have attempted to shed some light on the study of crystallization kinetics in polymer blends, as well as to point out some of the pitfalls that can occur when analysing kinetic data. It is clear from these results that a certain amount of caution should be exercised when applying the Lauritzen–Hoffman analysis to blend systems, since the original treatment was developed specifically for one-component systems. Furthermore, the modification of the Lauritzen–Hoffman equation, which incorporates entropic effects, may not be sufficient in all cases.

This study also points out a possible approach to solving one of the well-documented shortcomings of bacterial PHB, namely its melt-instability[52]. The blend system atactic/isotactic PHB represents a simple approach to lowering the melting point of the bacterial polymer without compromising its environmental qualities, since both components in the blend are biodegradable[53].

ACKNOWLEDGEMENTS

The authors thank Dr Steven Bloembergen, Polysar Rubber Corporation, for kindly supplying the atactic PHB. This work was supported by Xerox Corporation and the Natural Science and Engineering Research Council. R. Pearce thanks the Fonds Pour la Formation de Chercheurs et L'Aide à La Recherche (FCAR) and Paprican for scholarships.

REFERENCES

1 Keith, H. D. and Padden, F. J. *J. Appl. Phys.* 1964, **35**, 1286
2 Suzuki, T. and Kovacs, A. J. *Polym. J.* 1970, **1**, 82
3 Hoffman, J. D., Frolen, L. J., Ross, G. S. and Lauritzen, J. I. Jr *J. Res. Natl Bur. Std* 1975, **79A**, 671
4 Lovinger, A., Davis, D. D. and Padden, F. J. Jr *Polymer* 1985, **26**, 1595
5 Clark, E. J. and Hoffman, J. D. *Macromolecules* 1984, **17**, 878
6 Phillips, P. J. and Vatansever, N. *Macromolecules* 1987, **20**, 2138
7 Cheng, S. Z., Chen, J. and Janimak, J. J. *Polymer* 1990, **31**, 1018
8 Shi, G., Zhang, X. and Qiu, Z. *Makromol. Chem.* 1992, **193**, 583
9 Roitman, D. B., Marand, H., Miller, R. L. and Hoffman, J. D. *J. Phys. Chem.* 1989, **93**, 6919
10 Vasanthakumari, R. and Pennings, A. J. *Polymer* 1983, **24**, 175
11 Barham, P. J., Keller, A., Otun, E. L. and Holmes, P. A. *J. Mater. Sci.* 1984, **19**, 2781
12 Turnbull, D. and Fisher, J. C. *J. Chem. Phys.* 1949, **17**, 71
13 Hoffman, J. D. and Lauritzen, J. I. Jr *J. Res. Natl Bur. Std* 1961, **65A**, 297
14 Hoffman, J. D., Lauritzen, J. I. Jr, Passaglia, E., Ross, G. S., Frolen, L. J. and Weeks, J. J. *Koll. Zeitschr. Polym.* 1967, **231**, 564
15 Lauritzen, J. I. Jr and Hoffman, J. D. *J. Appl. Phys.* 1973, **44**, 4340
16 Hoffman, J. D., Davis, G. T. and Lauritzen, J. I. Jr in 'Treatise on Solid State Chemistry' (Ed. N. B. Hannay), Plenum Press, New York, 1976, Vol. 3, Ch. 7
17 Hoffman, J. D. *Polymer* 1982, **23**, 656
18 Hoffman, J. D. *Polymer* 1983, **24**, 3
19 Hoffman, J. D. *Polymer* 1985, **26**, 803
20 Hoffman, J. D. *Polymer* 1985, **26**, 1763
21 Hoffman, J. D. and Miller, R. L. *Macromolecules* 1988, **21**, 3038
22 Hoffman, J. D. *Macromolecules* 1989, **22**, 3502
23 Boon, J. and Azcue, J. M. *J. Polym. Sci., Part A-2* 1968, **6**, 885
24 Ong, C. J. and Price, F. P. *J. Polym. Sci., Polym. Symp.* 1978, **63**, 59
25 Wang, T. T. and Nishi, T. *Macromolecules* 1977, **10**, 421
26 Yeh, G. S. and Lambert, S. L. *J. Polym. Sci., Part A-2* 1972, **10**, 1183
27 Cimmino, S., Martuscelli, E., Silvestre, C., Canetti, M., DeLalla, C. and Seves, A. *J. Polym. Sci., Part B: Polym. Phys.* 1989, **27**, 1781
28 Amelino, L., Martuscelli, E., Sellitti, C. and Silvestre, C. *Polymer* 1990, **31**, 1051
29 Alfonso, G. C. and Russell, T. P. *Macromolecules* 1986, **19**, 1143
30 Marand, H. and Collins, M. *Polym. Prepr.* 1990, **31**, 552
31 Avella, M. and Martuscelli, E. *Polymer* 1988, **29**, 1731
32 Martuscelli, E., Sellitti, C. and Silvestre, C. *Makromol. Chem., Rapid Commun.* 1985, **6**, 125
33 Cimmino, S., Martuscelli, E. and Silvestre, C. *Makromol. Chem., Macromol. Symp.* 1988, **16**, 147
34 Martuscelli, E. and Silvestre, C. *Makromol. Chem.* 1989, **190**, 2615
35 Runt, J., Miley, D. M., Zhang, X., Gallagher, K. P., McFeaters, K. and Fishburn, J. *Macromolecules* 1992, **25**, 1929
36 Martuscelli, E., Silvestre, C. and Gismondi, C. *Makromol. Chem.* 1985, **186**, 2161
37 Martuscelli, E., Pracella, M. and Yue, W. P. *Polymer* 1984, **25**, 1097
38 Bonfatti, A. M., Canetti, M., Sadocco, P., Seves, A. and Martuscelli, E. *Polymer* 1993, **34**, 990
39 Dubini Paglia, E., Beltrame, P. L., Canetti, M. Seves, A., Marcandalli, B. and Martuscelli, E. *Polymer* 1993, **34**, 996
40 De Juana, R. and Cortázar, M. *Macromolecules* 1993, **26**, 1170
41 Marchessault, R. H., Coulombe, S., Morikawa, H., Okamura, K. and Revol, J. F. *Can. J. Chem.* 1981, **59**, 38
42 Pearce, R., Jesudason, J., Orts, W., Marchessault, R. H. and Bloembergen, S. *Polymer* 1992, **33**, 4647
43 Kumagai, Y. and Doi, Y. *Makromol. Chem., Rapid Commun.* 1992, **13**, 179
44 Hoffman, J. D. and Weeks, J. J. *J. Res. Natl Bur. Std* 1962, **66A**, 13
45 Bloembergen, S., Holden, D. A., Bluhm, T., Hamer, G. K. and Marchessault, R. H. *Macromolecules* 1989, **22**, 1656
46 Le Borgne, A., Spassky, N. and Sigwalt, P. *Polym. Bull.* 1979, **1**, 825
47 Runt, J. and Gallagher, K. P. *Polym. Commun.* 1991, **32**, 180
48 Williams, M. L. Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701
49 Hoffman, J. D., Miller, R. L., Marand, H. and Roitman, D. B. *Macromolecules* 1992, **25**, 2221
50 De Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, 1979
51 Point, J.-J., Damman, P. and Janimak, J. J. *Polymer* 1993, **34**, 3771
52 Holmes, P. A. in 'Developments in Crystalline Polymers' (Ed. D. C. Bassett), Elsevier, New York, 1988, Ch. 1
53 Jesudason, J., Marchessault, R. H. and Saito, T. *J. Envir. Polym. Degrad.* 1993, **1**, 89