Spherulitic Crystallization in Compatible Blends of Poly(vinylidene fluoride) and Poly(methyl methacrylate)

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ABSTRACT: Radial growth rates of spherulites in blends of poly(vinylidene fluoride) and poly(methyl methacrylate) have been measured at temperatures ranging from 115 to 157.5 °C. In the region of constant rate of growth, the rate decreases by as much as two orders of magnitude as the concentration of PMMA is increased from zero to 50% by weight. The effect is ascribed largely to changes in fluidity of the melt accompanying the wide variation of glass transition temperature of the system. Data are analyzed by incorporating changes in both glass temperature and melting point into a rate theory developed by Lauritzen and Hoffman for homopolymers. A good fit is attained for all blends with values of transport parameters that are common to a number of homopolymers.

In a previous study[1] of the compatibility of poly(vinylidene fluoride) (PVF_2) and poly(methyl methacrylate) (PMMA), the polymer pair was found to be miscible at temperatures near the melting point of PVF_2.[1-4] Upon cooling from the melt, however, PVF_2 was found either to crystallize or remain in the amorphous state depending upon cooling rate and melt composition. In a 50/50 (by weight) blend, for example, it was possible to supercool the melt to room temperature at a rate as low as 0.625 °C/min. This behavior had been ascribed to the compatible nature of the blends in the molten state and to wide variation in their glass transition temperatures (from about −50 °C for PVF_2[1,2] to about 95 °C for PMMA). A brief summary of glass temperatures and equilibrium melting points of PVF_2 in the blends is given in Table I.

Because of the relative ease with which the molten blends can be supercooled, this polymer pair provides a suitable medium for studying growth kinetics of spherulites, particularly in regard to the influence of the compatible uncrystallizable polymer in the blend. While spherulitic crystallization has been investigated in polymers blended with their atactic stereoisomers,[5,6] crystallization behavior in the PVF_2–PMMA system has a special appeal in that the two polymers are quite distinct in their chemical structures. Such a study has been carried out recently by Robeson[7] on blends of poly(ϵ-caprolactone) and poly(vinyl chloride). However, Robeson studied bulk crystallization kinetics in terms of tensile modulus.

Experimental Section

A PVF_2 resin, Kynar 821, was obtained from Pennwalt Corp. The PMMA was Acrylite H-12, supplied by the American Cyanamid Company. Their intrinsic viscosities and molecular weight distribution were reported in a previous publication.[1]

Cast films of PVf_2 and PVF_2–PMMA blends were prepared from *N,N*-dimethylformamide solutions of the polymers according to a procedure described earlier.[1] The average film thickness was about 0.1 mm. To prepare a typical specimen for microscopic observation, a piece about 5 × 5 mm in size was cut from the film, mounted on a cover slip along with a 50 μm thick aluminum shim, and covered with a 0.16 mm thick cover glass. The assembly was heated on a Reichert hot stage to 215 ± 1 °C and maintained there for about 10 min to allow any PVF_2 crystals in the sample to melt completely. The assembly was then pressed with a pair of tweezers to reduce the thickness of the sample to approximately that of the aluminum shim and transferred to a Mettler FP52 hot stage maintained at the desired crystallization temperature within ±0.2 °C. Calibration of the Mettler hot stage was accomplished by means of triple points of adipic acid (151.45 ± 0.05 °C) prepared in specimens matching the present sample geometry. Growing spherulites were photographed at appropriate intervals with a Polaroid camera attached to a Reichert polarizing microscope. Diameters of spherulites were measured using a scale obtained by photographing a stage micrometer (10 μm per division) under the same magnification in each run. X-ray analysis of the samples showed that virtually all PVF_2 crystals were in form II[8] regardless of the crystallization temperatures and composition employed in our study.

Results

Figures 1 and 2 show several time-sequence photographs of spherulites grown in the PVF_2 sample at 157.5 °C and in the PVF_2/PMMA = 67.5/32.5 (weight ratio) blend at 145 °C. In general the spherulites are seen to be more open in texture[5,9] when the blend is richer in PMMA concentration. In Figure 3 the diameter of the spherulite is plotted against time at a given crystallization temperature for several compositions. Except for a brief induction period which becomes more protracted for spherulites growing at a slower rate,[10,11] plot is clearly linear in the time span investigated. It was noted that at a given temperature, nucleation of spherulites was sporadic in time, but the spherulites grew at about the same rate once they were born in the melt.

Radial growth rates of spherulites in PVF_2 and its blends with PMMA are given in Figure 4 as a function of temperature. As with polyethylene,[5] spherulites in the undiluted PVF_2 nucleated profusely and grew at rapid rates, rising from 0.32 μm/min at 157.5 °C to 41 μm/min at 135 °C. Below 135 °C the spherulites were so numerous and small that it was not possible to measure growth rates accurately. The same difficulty was encountered in blends, but at lower temperatures; consequently, the data for each composition tend to suffer larger scatter at the lower temperature end.

There is a dramatic reduction in growth rates on addition of PMMA to the crystallizable polymer. At 135 °C, for example, the growth rate falls sharply from 41 μm/min for PVF_2 to 0.29 μm/min for the 55/45 blend. The influence of the noncrystallizable diluent here is much stronger than that observed by Keith and Padden and Yeh and Lambert for isotactic polystyrene[5,6] and isotatic polypropylene[5] diluted with their atactic species. However, as with the stereoregular–irregular pairs, there appears to be a slight shift in the growth maximum to a higher temperature with the increase in the PMMA content. The ratio of the maximum-growth temperature to the equilibrium melting point $T_m°$ (Table I) is about 0.87 for the 75/25 mixture and it increases to 0.90 for the 50/50 blend. These values are in good accord with those reported in the literature[10,12] for a variety of homopolymers.

Discussion

In general the steady state growth rate of spherulites can be qualitatively described by the modified Turnbull–Fisher equation originally derived for monoatomic substances,

$$G = G_0 \exp(-\Delta\phi^*/kT) \exp(-\Delta F^*/kT) \qquad (1)$$

where T is the crystallization temperature, k is Boltzmann's

Table I
Equilibrium Melting Points, T_m°, and Glass Temperatures, T_g, for PVF$_2$ and Its Blends with PMMA

	T_m°, °C[a]	T_g, °C[b]
PVF$_2$	173.8	−50
PVF$_2$/PMMA = 82.5/17.5	172.1	−15
PVF$_2$/PMMA = 75/25	170.5	0
PVF$_2$/PMMA = 67.5/32.5	168.6	14
PVF$_2$/PMMA = 55/45	164.8	39
PVF$_2$/PMMA = 50/50	163.2	45

[a] Determined by the extrapolation method of Hoffman and Weeks.[10] [b] Measured by differential scanning calorimetry at 10 °C/min after samples had been quenched from the melt in liquid nitrogen.

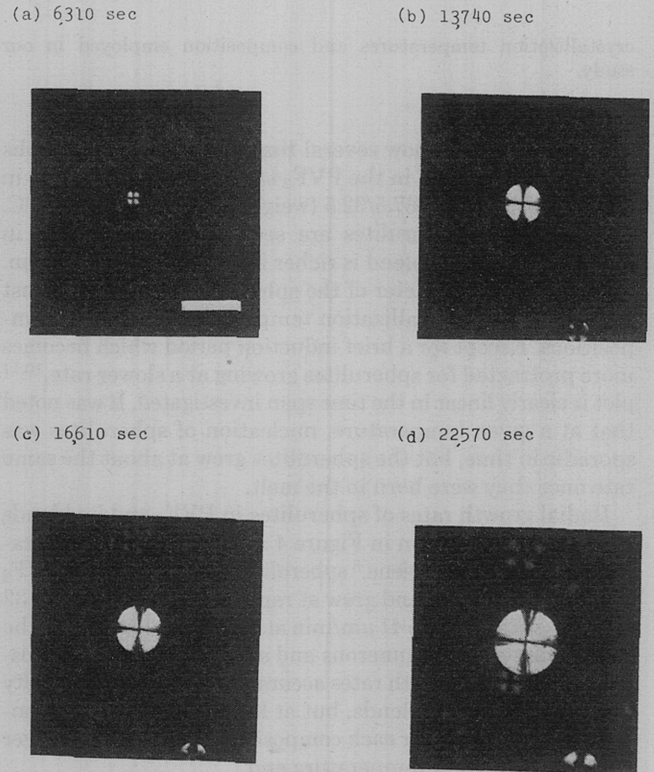
(a) 6310 sec (b) 13740 sec (c) 16610 sec (d) 22570 sec

Figure 1. Spherulites grown in PVF$_2$ at 157.5 °C for different time periods. White bar in (a) corresponds to a length of 100 μm.

constant, $\Delta\phi^*$ is the free energy required to form a critical-sized nucleus from the melt, ΔF^* is the activation energy for transport of crystallizing units across the liquid–crystal interface, and G_0 is a constant. The equation has been refined recently by Lauritzen and Hoffman (LH)[13] using a molecular model appropriate to crystallization of homopolymers over a wide range of undercoolings. The mathematical form of the LH expression is basically similar to eq 1. But the term $\exp(-\Delta F^*/kT)$ is replaced with a modified segmental jump rate term $\exp[-U^*/R(T - T_\infty)]$ on the assumption that the latter dominates in the crystallization of polymers.[10,14] U^* is the activation energy for transport of crystallizable segments through the melt to the site of crystallization. T_∞ is a hypothetical temperature where all molecular motion associated with viscous flow ceases and is related to T_g by $T_\infty = T_g - C$ where C is a constant. The free energy $\Delta\phi^*$ takes two different forms depending on the manner by which the surface nuclei are formed and spread on an existing crystal face. The LH expression was subsequently applied by Hoffman, Davis, and Lauritzen[15] with remarkable success to a large number of homopolymers over a wide range of temperature.

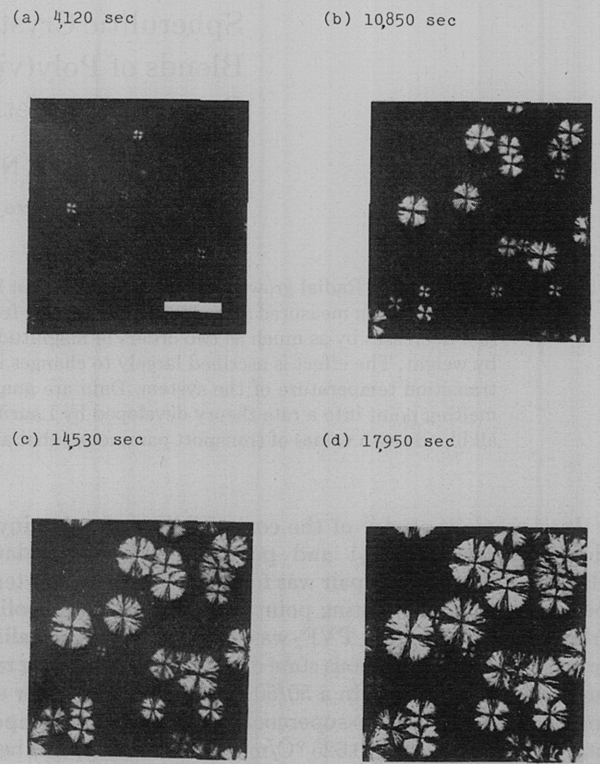
(a) 4120 sec (b) 10850 sec (c) 14530 sec (d) 17950 sec

Figure 2. Spherulites grown in the PVF$_2$/PMMA = 67.5/32.5 blend at 145 °C for different time periods. White bar in (a) corresponds to a length of 100 μm.

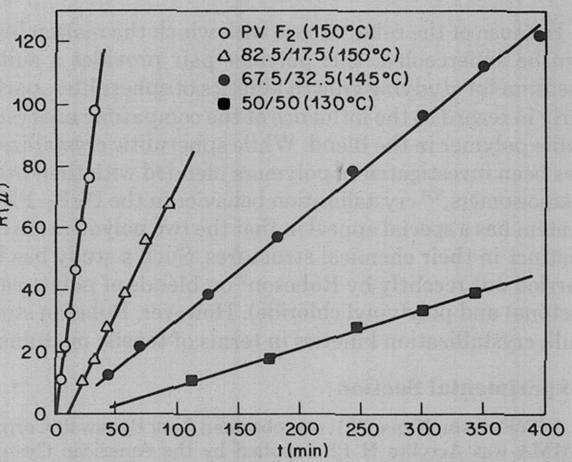

Figure 3. Graph showing diameter as a function of time for spherulites in PVF$_2$ and its blends with PMMA at various temperatures.

For polymer blends where crystallization of one polymer takes place in the presence of a noncrystallizable component, growth rates are influenced not only by the initial composition of the blend but also by local changes of composition in the melt due to rejection of noncrystallizable species from crystals.[5] Rejected species, however, are not limited to segments of the polymeric diluent only since short-chain fractions are always present in the crystallizing polymer and these also tend to remain in the melt phase. Since growth rate is primarily governed by the composition of the melt at the growth front, build up of a depletion layer (containing a low concentration of crystallizable polymer) at the interface could affect the rates of growth in two significant ways. First, depending on the

Table II
Values of K_g, G_0, $\sigma\sigma_e$, σ_e, and q from Data Analysis

PVF_2/PMMA	v_2	$K_g \times 10^5$, K^2	G_0, cm/s	Corr coeff	$\sigma\sigma_e$, erg^2/cm^4	σ_e, erg/cm^2	q, kcal/mol of folds
100/0	1	0.669	0.182	0.9991	463.7	47.5	3.31
82.5/17.5	0.762	0.692	0.141	0.9978	478.8	49.1	3.42
75/25	0.671	0.714	0.131	0.9993	495.5	50.8	3.54
67.5/32.5	0.585	0.701	0.0887	0.9997	488.7	50.1	3.49
55/45	0.453	0.660	0.0561	0.9988	463.9	47.5	3.31
50/50	0.404	0.561	0.0125	0.9992	395.7	40.5	2.82

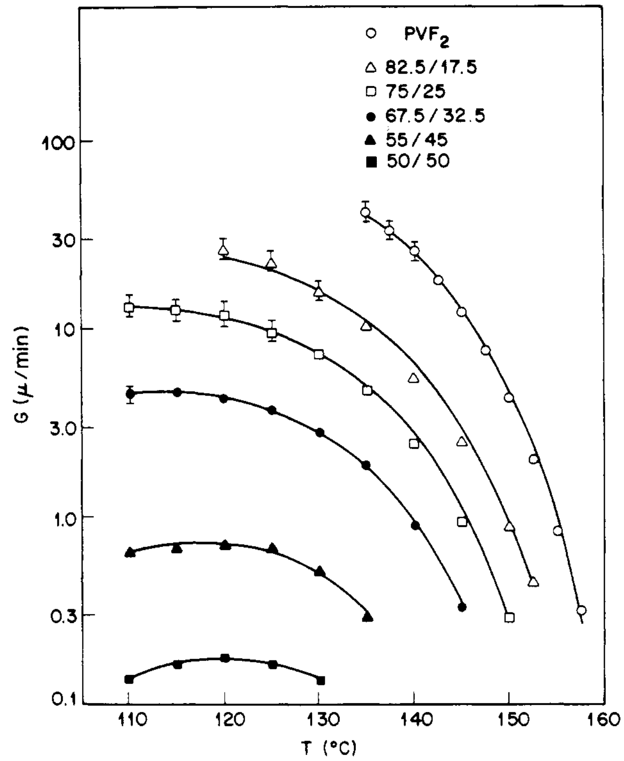

Figure 4. Radial growth rate G ($=dR/dt$) of spherulites in PVF_2 and its blends with PMMA at various temperatures. Solid curves represent growth rates calculated from eq 2 using values of U^*, T_∞, and G_0 obtained in the data analysis.

nature and concentration of the rejected material, it could either retard or promote rates of transport of crystallizable species to the growth sites. This effect should become increasingly important at larger undercoolings where rates of growth are dominated by a diffusive transport process. Second, it could systematically depress the melting point of the blend at the growth front, thereby reducing the rate of nucleation. The composition of the melt at this front is in turn influenced by the initial composition of the blend, the diffusion coefficient of the melt in the depletion layer, and the growth rate. A rigorous treatment of such a complex problem presents considerable difficulty and without simplifying assumptions an explicit expression for growth rate cannot be obtained.[5]

For blends of PVF_2 and PMMA which are compatible in the molten state and exhibit a wide variation of T_g with composition (e.g., $T_g = -50$ °C for PVF_2 and 45 °C for the 50/50 blend),[1] the marked dependence of growth rates on composition may be primarily due to changes in viscosity of the melt brought about by changes in initial composition. In blends of isotactic and atactic polystyrenes whose T_g remains invariant, the influence of changes in concentration is relatively mild and almost linear[5,6] while in the system of poly(vinyl chloride)–poly(ε-caprolactone), which exhibits a wide variation in T_g, a marked dependence of growth rate on composition is observed.[7,16] Accordingly, our approach will be to examine if the corresponding growth behavior in PVF_2–PMMA blends can be accounted for approximately by incorporating changes in both glass temperature and melting point into the LH expression.

The original LH expression for homopolymers is,

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

where G_0, U^*, and T_∞ are defined as before and K_g is a nucleation parameter independent of crystallization temperature. The explicit form of K_g, which contains surface free energies, heat of fusion, and melting point, will be discussed in detail subsequently. $\Delta T = T_m° - T$, and $f = 2T/(T_m° + T)$ is a correction factor for the bulk free-energy difference between the supercooled liquid and the crystal, Δf at large undercoolings.[10]

For the present purpose, G_0 is assumed to be a function of the initial volume fraction of PVF_2, v_2, and $T_m°$ and T_g are to be identified with the equilibrium melting point and the glass temperature of the blend. Thus, for $v_2 = 1$, $T_m°$ and T_g refer to the homopolymer PVF_2 and the original LH theory applies. Effects of the above assumption on the bulk free energy of the blend, $\Delta f(v_2)$, are discussed in the Appendix. It is shown that when melting point depression is small compared to $T_m°$, replacement of $T_m°$ of PVF_2 by $T_m°$ of the blend does not alter the value of $\Delta f(v_2)$ and hence the values of K_g and f in eq 2. By identifying v_2, $T_m°$, and T_g with those of the blend, rather than with those of the depletion layer, we have in effect assumed that the consequences of compositional changes at growth fronts are insignificant as compared with those due to initial dilution. This is probably not unreasonable for blends of moderate to low dilution crystallized at temperatures such that transport properties do not have a preponderant influence on kinetics. We will make further comments on this following an analysis of the growth rate data.

According to eq 2 a plot of $\ln(G) + U^*/R(T - T_\infty)$ against $1/T(\Delta T)f$ should yield a straight line with an intercept $\ln(G_0)$ and a slope ($-K_g$). Hoffman, Davis, and Lauritzen[15] found that eq 2 accurately fits the growth rate data of a number of polymers with a value of U^* in the vicinity of 1500 cal/mol and a value of C close to 30 K. Using an expression essentially equivalent to that of LH, Suzuki and Kovacs[17] similarly obtained an excellent fit for isotactic polystyrene with $U^* = 1560$ cal/mol and $C = 30$ K. These results suggest an initial range of values for U^* and C for use in our trial plots. An analysis using a least-squares scheme shows that data for each composition can be fitted closely with $U^* = 1500$ cal/mol and $C = 30$ K. Results for $G_0(v_2)$ and K_g are listed in Table II along with the correlation coefficients attained in the least-squares fit. The solid curves in Figure 4 represent the growth rates calculated from eq 2 using values of $G_0(v_2)$ and K_g in Table II. The values of $G_0(v_2)$ and K_g in Table II fall within the ranges obtained by Hoffman, Davis, and Lauritzen[15] and Suzuki and Kovacs[17] for a variety of homopolymers.

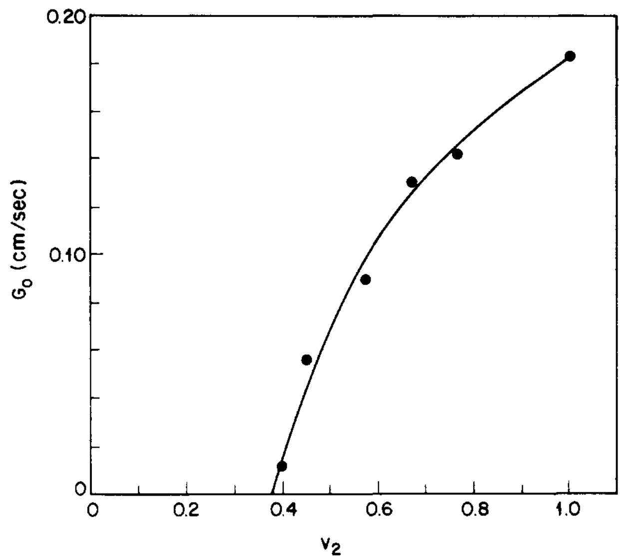

Figure 5. Plots of the preexponential factor G_0 of PVF$_2$–PMMA blends vs. volume fraction of PVF$_2$, v_2.

The results of the foregoing data analysis merit some comments in view of the simplifying assumptions we made in eq 2 for application to polymer blends. The excellent fit attained in our analysis is due, at least in part, to the flexibility of the four-parameter LH expression. While it is remarkable that the data for all blends can be fitted with the same values of U^* and C, it is worth noting that only a limited number of data are available at temperatures below the temperature of maximum growth (Figure 4). A test of our approach in this region where the influence of the transport term is predominant would have been more conclusive. This is not possible with our PVF$_2$–PMMA blends because, as noted earlier, spherulites nucleate profusely and grow at a rapid rate at low temperatures. If it should turn out that the analysis is still valid, it would mean that changes in T_g and $T_m{}^\circ$ due to initial changes in composition are primarily responsible for the composition dependence of the growth rate. However, compositional changes in the melt during crystallization are very real and while their relative importance cannot be determined for our blends, the unusually good fit cannot be accepted without caution.

In Figure 5 the preexponential factors $G_0(v_2)$ for the blends are plotted against the volume fraction of PVF$_2$, v_2. For $v_2 = 0.671$ (75/25 blend) or higher, G_0 changes mildly with v_2. At lower v_2, however, G_0 falls rapidly with the decrease in v_2. The sharp decline of G_0 in diluted blends is probably due to the influence of compositional changes in the melt at the growth front. Aside from the possible influence of compositional changes in the melt, G_0 is known to be strongly dependent on a number of factors[14,17] which are not readily assessable with our present results.

The values of K_g for the blends allow the apparent lateral and end surface free energies, σ and σ_e, to be calculated from the following formulas,[13]

$$K_{g(I)} = 4b_0(\sigma\sigma_e)T_m{}^\circ/(\Delta h_f)k \qquad (3)$$

$$K_{g(II)} = 2b_0(\sigma\sigma_e)T_m{}^\circ/(\Delta h_f)k \qquad (4)$$

Here b_0 is the thickness of a monomolecular layer in the crystal, $K_g = K_{g(I)}$ if the formation of a surface nucleus is followed by rapid completion of the substrate (regime I kinetics), and $K_g = K_{g(II)}$ if surface nuclei form in large number on the substrate and spread slowly (regime II kinetics). The conditions where regime I and regime II apply are found by using the Z test of Lauritzen.[18] Z is defined by

$$Z \simeq 10^3(L/2a_0)^2 \exp[-X/T(\Delta T)] \qquad (5)$$

where L is the effective lamellar width and a_0 is the width of the molecular chain in the crystal. If substitution of K_g value for X in eq 5 results in $Z \leq 0.01$, then crystallzation conforms to regime I. On the other hand if, with $X = 2K_g$, eq 5 yields $Z \geq 1$, regime II kinetics is obeyed. In practice, as pointed out by Lauritzen and Hoffman,[13] it is more convenient to use the known value of K_g and the inequalities for Z to estimate the range of values of L in regime I or regime II and determine if these L values are realistic in each regime.

Application of the Z test to the data of PVF$_2$–PMMA blends shows that for crystallization to occur in regime I, L cannot be more than 4.4 Å for the entire ranges of composition and temperature investigated. This is clearly unrealistic. Similar tests for regime II show that L should be greater than a few tens to a few hundreds of ångströms for $T \leq 155$ °C and a few thousands of ångströms at higher temperatures. We therefore conclude that growth in blends takes place by multiple nucleation acts and K_g takes the form of $K_{g(II)}$ in eq 4. In retrospect, this result is not surprising from morphological considerations since the formation of thin depletion layers at growth fronts during spherulitic crystallization causes an instability of the crystal surface profile and favors multiple nucleation events.[9]

For the samples used, PVF$_2$ crystals are of form II[1] with metrically orthorhombic unit cells (all anges = 90°), the lattice constants being $a = 5.02$ Å, $b = 9.63$ Å, and $c = 4.62$ Å at 20 °C.[19] The thickness of a monomolecular layer, b_0, in the (110) plane is 4.45 Å and the chain width, a_0, is 5.43 Å. Using these values as approximate chain dimensions at elevated temperatures and $\Delta h_f = 1.986 \times 10^9$ erg/cm^2,[20] values for the products, $\sigma\sigma_e$, of the blends are calculated from eq 4 and listed in Table II.

Following the procedure of Hoffman, Davis, and Lauritzen,[15] the end-surface free energy, σ_e, and the work required to form a fold, q, are determined from the values of $\sigma\sigma_e$ in Table II using the relationships

$$\sigma = 0.1(\Delta h_f)(a_0b_0)^{1/2} = 9.76 \text{ erg/cm}^2 \qquad (6)$$

$$\sigma_e = (\sigma\sigma_e)/\sigma \qquad (7)$$

$$q = 2a_0b_0\sigma_e \qquad (8)$$

and the results are presented in Table II. It may be seen that, except for the 50/50 blend, the value of σ_e remains reasonably constant for all compositions. This is perhaps not surprising since the concentration-dependent part of the surface energy is only a few ergs per square centimeter which is much smaller than the energy required for chain folding. The values of σ_e and q appear to be in a reasonable range when compared with those of other homopolymers[15] (e.g., σ_e and q are respectively 93 erg/cm^2 and 5.5 kcal/mol of folds for polyethylene, 35 erg/cm^2 and 7 kcal/mol of folds for isotactic polystyrene).

Nakagawa and Ishida[20] have found an "equilibrium" σ_e value of 146 erg/cm^2 (10.2 kcal/mol of folds) from plots of T_m vs. reciprocal of lamellar thickness for PVF$_2$. By comparison, our kinetically determined value for PVF$_2$, 47.5 erg/cm^2, is much lower. The difference appears to be too large even if consideration is given to errors that could result from fitting the relatively small number of data for PVF$_2$ (see Figure 4).[15] It is also noteworthy that our "kinetic" value for the homopolymer was obtained directly from the original LH theory and therefore is not subject to approximations made in our treatment on blends. In the same plots for determination of σ_e, Nakagawa and Ishida obtained an equilibrium melting point of 210 °C which was apparently too high for the form II crystals as indicated in a subsequent paper[22] ($T_m° = 188$ °C). Measurements by Prest and Luca[23] and by us[1] also gave a lower equilibrium melting point (~173 °C). It is likely that the samples used by Nakagawa and Ishida,[20] which were subjected to sequences of quenching and annealing at various temperatures, contained fractions of high-melting form III crystals. This would raise the value of σ_e because form III crystals grow only at high annealing temperatures (>160 °C) where thickening of lamellae is likely to occur.

Conclusions

Radial growth rates of spherulites in blends of PVF_2 and PMMA are found to fall by as much as two orders of magnitude as the weight fraction of PMMA is increased from 0 to 50%. Factors which could give rise to such a marked composition dependence include: the presence of depletion layers at growth fronts, melting point depression, and the large variation in T_g due to changes in composition. On the assumption that changes in viscosity of the melt accompanying changes in T_g are primarily responsible for the observed composition dependence, data are analyzed by incorporating changes in T_g and $T_m°$ of the system into a rate theory developed by Lauritzen and Hoffman for homopolymers. The data can be fitted closely with values of transport parameters which are common to a number of homopolymers. However, more data may be needed to verify whether or not it would hold at lower temperatures. The preexponential factor G_0 is a nonlinear function of initial volume fraction of PVF_2 in the blend. In keeping with morphological considerations, growth of PVF_2 crystals in the blends is found to conform to regime II kinetics. Values of nucleation parameters U^*, T_∞, σ, σ_e, and q for PVF_2 and its blends with PMMA are in a reasonable range when compared with values determined for other homopolymers.

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Appendix

We consider a two-dimensional coherent nucleation process which involves the monomolecular deposition of chain units on an already existing crystal surface. The change in free energy that accompanies the formation of such a surface nucleus with fixed thickness b_0 and length l in a crystalline polymer–amorphous polymer system (ignoring chain end effects) is

$$\Delta\phi = 2a_0b_0\sigma_e + 2lb_0\sigma - a_0b_0l\Delta f(v_2) \qquad \text{(A1)}$$

where a_0 is the width of the nucleus and $\Delta f(v_2)$ is the bulk free energy difference per unit volume of crystal between the supercooled liquid and the crystal. For this polymer–polymer mixture, $\Delta f(v_2)$ can be expressed in the following form,[1]

$$\Delta f(v_2) = \Delta f + A\frac{RTV_{2u}}{V_{1u}} \times \left[\frac{\ln v_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right)(1 - v_2) + \chi_{12}(1 - v_2)^2\right] \qquad \text{(A2)}$$

where Δf is the bulk free energy per unit volume of PVF_2 crystal at T, V_u is the molar volume of the repeating unit, m is essentially the degree of polymerization,[24] χ_{12} is the polymer–polymer interaction parameter, and A is a unit conversion factor.

For T close to $T_m°$, the equilibrium melting temperature of PVF_2, we have

$$\Delta f \cong \Delta h_f\left(\frac{T_m° - T}{T_m°}\right) \qquad \text{(A3)}$$

and[1]

$$\frac{1}{T_m} - \frac{1}{T_m°} = -\frac{AV_{2u}}{\Delta h_f V_{1u}}\left[\frac{\ln v_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right)(1 - v_2) + \chi_{12}(1 - v_2)^2\right] \qquad \text{(A4)}$$

where T_m is the equilibrium melting temperature of the mixture and Δh_f is the heat of fusion per unit volume of the crystal.

Substitution of (A3) and (A4) into (A2) yields,

$$\Delta f(v_2) = \Delta h_f\left(\frac{T_m - T}{T_m}\right) \qquad \text{(A5)}$$

For large supercoolings, $T \ll T_m°$, Hoffman[10] suggests a better approximation for Δf,

$$\Delta f \simeq \Delta h_f\frac{T_m° - T}{T_m°}\left(\frac{2T}{T_m° + T}\right) \qquad \text{(A6)}$$

If this expression for Δf is used in the derivation of the melting point depression for the blend,[1] the resulting expression together with (A6) yields for $\Delta f(v_2)$,

$$\Delta f(v_2) = \Delta h_f\frac{2T}{T_m°}\left[\frac{T_m° - T}{T_m° + T} - \frac{T_m° - T_m}{T_m° + T_m}\right] \qquad \text{(A7)}$$

Since the melting point depression $\Delta T_m = (T_m° - T_m)$ of the system is small in the range of composition investigated,[1] $\Delta T_m \ll T_m°$, and (A7) can be approximated by

$$\Delta f(v_2) = \Delta h_f\frac{T_m - T}{T_m}\left(\frac{2T}{T_m + T}\right) \qquad \text{(A8)}$$

References and Notes

(1) T. Nishi and T. T. Wang, *Macromolecules*, **8**, 909 (1975).
(2) J. S. Noland, N. N.-C. Hsu, R. Saxon, and J. M. Schmitt, *Adv. Chem. Ser.*, **99**, 15 (1971).
(3) D. R. Paul and J. O. Altamirano, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **15**, 409 (1974).
(4) G. D. Patterson, T. Nishi, and T. T. Wang, *Macromolecules*, **9**, 603 (1976).
(5) (a) H. D. Keith and F. J. Padden, Jr., *J. Appl. Phys.*, **35**, 1270 (1964); (b) *ibid.*, **35**, 1286 (1964).
(6) G. S. Y. Yeh and S. L. Lambert, *J. Polym. Sci., Part A-2*, **10**, 1183 (1972).
(7) L. M. Robeson, *J. Appl. Polym. Sci.*, **17**, 3607 (1973).
(8) J. B. Lando, H. G. Olf, and A. Peterlin, *J. Polym. Sci., Part A-1*, **4**, 941 (1966).
(9) H. D. Keith and F. J. Padden, Jr., *J. Appl. Phys.*, **34**, 2409 (1963).
(10) J. D. Hoffman and J. J. Weeks, *J. Chem. Phys.*, **37**, 1723 (1962).
(11) F. P. Price, *J. Am. Chem. Soc.*, **74**, 311 (1952).
(12) L. Mandelkern, "Crystallization of Polymers", McGraw-Hill, New York, N.Y., 1964.
(13) J. I. Lauritzen, Jr., and J. D. Hoffman, *J. Appl. Phys.*, **44**, 4340 (1973).
(14) J. D. Hoffman, *SPE Trans.*, **4**, 1 (1964).
(15) J. D. Hoffman, G. T. Davis, and J. I. Lauritzen, Jr., "Treatise on Solid State Chemistry", Vol. 3, N. B. Hannay, Ed., Plenum Press, New York, N.Y., 1976, Chapter 6. See also, J. D. Hoffman, L. J. Frolen, G. S. Ross, and J. I. Lauritzen, Jr., *J. Res. Natl. Bur. Stand., Sect. A*, **79**, 671 (1975).
(16) J. C. Ong, Ph.D. Thesis, University of Massachusetts, 1973.
(17) T. Suzuki and A. Kovacs, *Polym. J.*, **1**, 82 (1970).
(18) J. I. Lauritzen, Jr., *J. Appl. Phys.*, **44**, 4353 (1973).
(19) W. W. Doll and J. B. Lando, *J. Macromol. Sci., Phys.*, **4**, 309 (1970).
(20) K. Nakagawa and Y. Ishida, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 2153 (1973).
(21) T. W. Huseby and H. E. Bair, *J. Appl. Phys.*, **39**, 4969 (1968).
(22) S. Osaki and Y. Ishida, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 1071 (1975).
(23) W. M. Prest and D. J. Luca, *J. Appl. Phys.*, **46**, 4136 (1975).
(24) R. L. Scott, *J. Chem. Phys.*, **17**, 279 (1949).