IBM-San Jose for the gel permeation chromatograph measurements, Dr. J. Heller of Stanford Research Institute for his advice on anionic polymerization, and Drs. J. D. Ferry and J. L. Schrag for their comments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Office of Naval Research for the support of this research.

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Melting Point Depression and Kinetic Effects of Cooling on Crystallization in Poly(vinylidene fluoride)–Poly(methyl methacrylate) Mixtures

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ABSTRACT: Thermal analysis of solution cast mixtures of poly(vinylidene fluoride) (PVF_2) and poly(methyl methacrylate) (PMMA) has been carried out with various programmed temperature profiles. Results from experiments conducted in a quasi-equilibrium state show that PVF_2 crystallizes in the mixture upon cooling. Furthermore, depressions were observed in the melting and the crystallization temperatures. The melting point depression phenomenon is found to be explicable in terms of thermodynamic mixing of a crystalline polymer with an amorphous polymer. To this end, an analytical expression appropriate to the crystalline–amorphous polymer pair is derived from Scott's equation for thermodynamic mixing of two polymers. From this expression the interaction parameter for the polymer pair is found to be −0.295 at 160°C, indicating that the system is compatible in the molten state. The depression of crystallization temperature which depends strongly on both the composition and the cooling rate is attributed to the ability of the PVF_2 segments to migrate and to the change of composition in the melt during crystallization. For mixtures with a PVF_2 content by weight of less than 0.5, it is possible to suppress the crystal transformation at room temperature with a moderate cooling rate. Finally, it is pointed out that because of the strong kinetic effects of cooling on the thermodynamic state of the mixture, caution should be exercised in the calorimetric study of compatibility of the polymer pair.

In previous studies[2] concerned with compatibility of polymer–polymer systems it has been found helpful to interpret the miscibility of the mixtures in terms of their phase diagrams. It has also been shown that the thermal history of the mixture has a pronounced effect on the mixing behavior of the polymer pair when the experimental temperature approaches or falls below the glass transition temperature of the mixture.[3,4] These studies have been confined so far to the amorphous polymer pair or, in the case of a crystalline–amorphous polymer pair, the mixing of amorphous fraction of the crystalline polymer and the amorphous polymer. An examination of the compatibility between a crystalline polymer and an amorphous polymer therefore becomes a natural extension of our general study.

Recently, it was reported in the literature that poly(vinylidene fluoride) (PVF_2) and poly(methyl methacrylate) (PMMA) form a compatible mixture when blended in the melt.[5–9] It was also reported that PVF_2 crystallizes in the

Table I
Molecular Weight Distribution Data for Poly(vinylidene fluoride) (PVF_2) and Poly(methyl methacrylate) (PMMA) Samples[a]

	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_z/\overline{M}_w$
PVF_2	215800	404300	661000	1.87	1.63
PMMA	36600	91500	170000	2.50	1.86

[a] $\overline{M}_n$, $\overline{M}_w$, and $\overline{M}_z$ represent number, weight, and z average molecular weights calculated from gel permeation chromatography calibrated with the polystyrene standard.

mixture when the weight fraction of the polymer is more than 0.5.[5,6] Similar results have been observed in another polymer pair, poly(ϵ-caprolactone)–poly(vinyl chloride).[10,11] In both systems, the depression of melting point was observed[5,6,11] although the phenomenon was not elaborated in detail.

In this paper a calorimetric study is made on the PVF_2–PMMA mixtures under various heating and cooling programs. Specifically the glass transition temperature and melting and crystallization behavior of the mixture are analyzed with a view toward understanding the compatibility behavior of the polymer pair.

Experimental Section

Materials: A poly(vinylidene fluoride) (PVF_2) resin, Kynar 821, in powder form was obtained from the Pennwalt Corp. The poly(methyl methacrylate) (PMMA) was Acrylite H-12 supplied by the American Cyanamid Co. in pellet form.

The intrinsic viscosity of the polymer in *N,N*-dimethylformamide (DMF) at 25°C was found to be 1.45 dl/g for PVF_2 and 0.303 dl/g for PMMA. The molecular weight distribution data determined from gel permeation chromatography using polystyrene as the calibration standard are listed in Table I.

Preparation of Samples. Films of PVF_2, PMMA, and their mixtures were cast from DMF solution onto a glass surface at room temperature. Throughout this paper, the ratio of PVF_2 to PMMA in the mixture is reported on a weight basis. The initial concentration of each polymer in DMF was about 3 g/100 ml. After the film was cast, DMF was allowed to evaporate very slowly under a stream of air at a reduced pressure (ca. ⅓ atm) for at least 1 week. The resulting films were subjected to further drying under vacuum at a temperature about 30°C or more above their glass transition temperatures for 1 week and slowly cooled to room temperature. The average film thickness was about 0.02 cm. X-ray analysis of the sample indicated that virtually all PVF_2 crystals were in form II[12-14] regardless of the thermal treatments used in our study. The homogeneity of the mixture in the molten state was studied with Brillouin light scattering and found to be homogeneous on a molecular scale.[15]

Heat Treatment and Measurement of Thermal Properties. A Perkin-Elmer Model DSC-1B differential scanning calorimeter was used for heat treating the samples and for the calorimetric study under several temperature conditions to be described below. In each test, the sample weighed 20.0 mg. The temperature readings were calibrated with indium (mp 156.3°C), naphthalene (mp 80.3°C), and anthraquinone (mp 284.2°C) at each heating rate employed in the measurements.

The heating (cooling) programs used for the DSC study and the heat treatment are illustrated in Figure 1. Program (a), with a heating rate of 10°C/min, was used for studying the thermal behavior of the as-cast samples. Program (b) was used for studying the effects of isothermal crystallization of the as-cast samples. Under this program the samples were maintained at 200°C for at least 30 min to ensure complete melting of the PVF_2 crystals before being cooled at 10°C/min to the crystallization temperature, T_c. Following the crystallization treatment at T_c, which lasted 17 to 65 hr, the samples were cooled to room temperature at 10°C/min. In the last cooling run, thermograms of the samples were obtained to monitor any trace of secondary crystallization. Throughout the measurements in which T_c was varied from 95°C for the PVF_2/PMMA = 50/50 mixture to 160°C for pure PVF_2, there was no evidence of secondary crystallization. In the final leg of program (b) the melting temperatures of the isothermally crystallized samples were measured at the heating rate of 10°C/min.

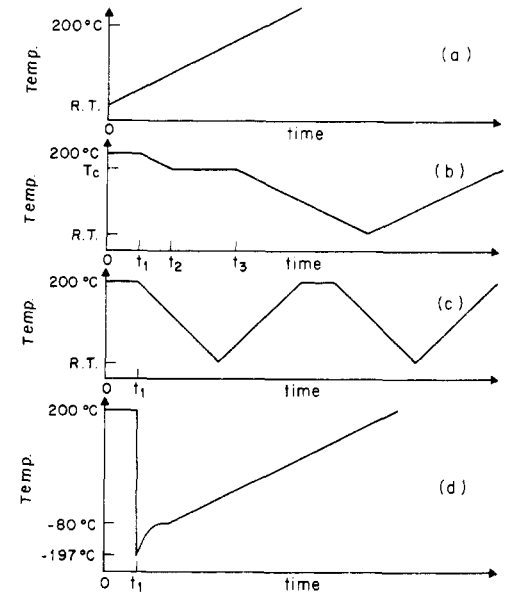

Figure 1. Thermal programs used for differential scanning calorimetry and heat treatment of the samples.

Program (c) was intended for observing the effects of cooling and heating rates on crystallization and melting of the polymer blends. The as-cast samples were at first conditioned at 200°C for 30 min. Then, as the samples were being cooled at a given rate, their crystallization behavior was observed. After the samples were cooled to room temperature, they were heated, at the same rate as in cooling, to 200°C for observation of their melting behavior. This temperature cycle was repeated several times. Reproducibility of the data was found to be satisfactory after the first cycle. The heating and cooling rates used in this study ranged from 0.625 to 40°C/min.

Program (d) was used to study the effects of quenching on the thermal behavior of the as-cast samples. The samples were quenched in a liquid nitrogen bath after conditioning at 200°C for 30 min. As soon as quenching was completed, the samples were transferred to a DSC pan maintained at −80°C and heated at a constant rate to a maximum temperature of 200°C while their glass transition, crystallization, and melting behavior were monitored. Although a heating rate of 10°C/min was used for most samples, those which showed distinct crystallization behavior were further studied at different heating rates.

Results

(a) Solution-Cast Samples. Figure 2 displays several examples of the thermograms for PVF_2, PMMA, and their mixtures measured at the heating rate of 10°C/min. It is apparent from the melting endotherms that PVF_2 is partially crystalline in the mixture even at low PVF_2 concentration. Furthermore, there is clear evidence of the depression of the melting point of PVF_2 crystals in the mixtures. Figures 3 and 4 show how the melting temperature T_m, the glass transition temperature T_g, and the total endotherm area due to the melting of crystalline PVF_2 depend on the weight fraction (ϕ_w) of PVF_2 in the mixture. The melting point, T_m, is determined by the usual method[16] which locates the temperature at which the last detectable trace of crystallinity disappears, and T_g is defined as the onset of a jump in the specific heat on heating as observed from the thermogram. The melting point T_m of pure PVF_2, at 170.6°C, is consistent with data measured by others.[6,17] On the other hand, the melting point of the mixture PVF_2/PMMA = 17.5/82.5 is 147.6°C which is about 23°C lower than that of pure PVF_2.

There is at most a feeble sign of dependence of T_g on ϕ_w; if any, T_g appears to increase slightly with the decrease in ϕ_w. The broken line in Figure 4 represents the limiting case where there is no interaction between the components and

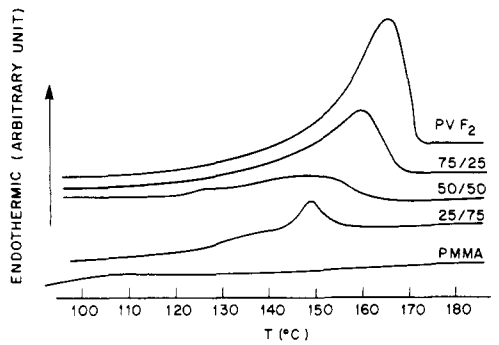

Figure 2. Thermograms of solution-cast PVF_2, PMMA, and some of their mixtures obtained at the heating rate of 10°C/min.

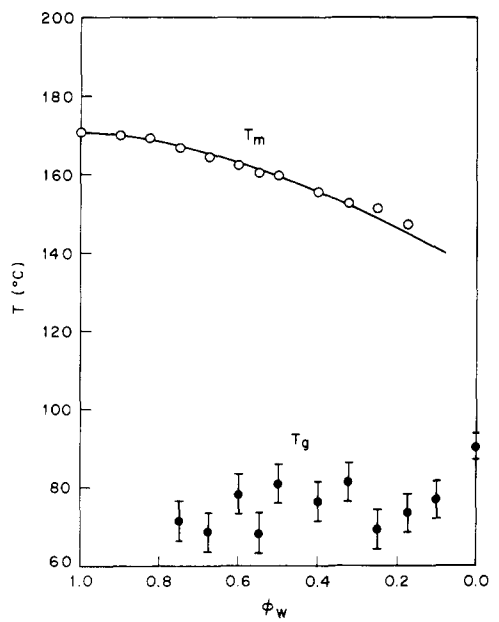

Figure 3. Dependence of melting temperature (T_m) and glass transition temperature (T_g) of the solution-cast mixture on the weight fraction of (ϕ_w) PVF_2.

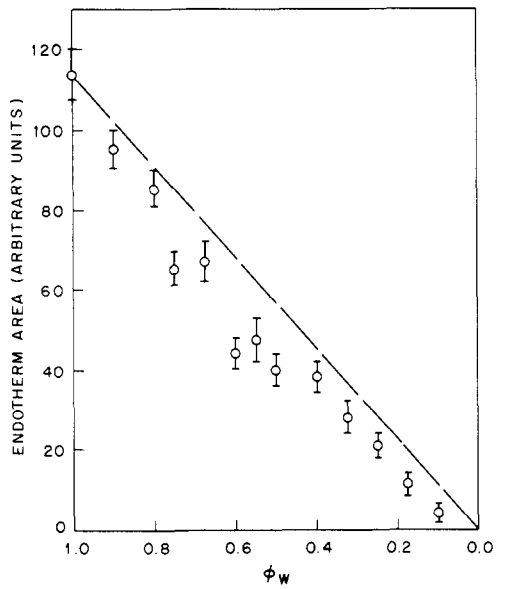

Figure 4. Dependence of the endotherm area due to the melting of PVF_2 crystals in the solution-cast mixture on the weight fraction (ϕ_w) of PVF_2.

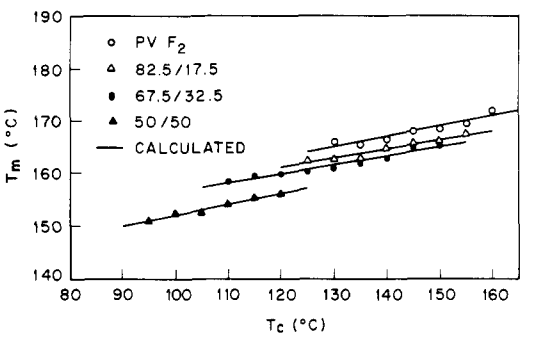

Figure 5. A plot of the melting temperature (T_m*) of PVF_2 crystals in the mixtures vs. the crystallization temperature (T_c).

PVF_2 is assumed to have completely crystallized from the mixture. It is of interest to note that these data differ markedly from those of melt-mixed systems[5,6] where melting of crystalline PVF_2 is not observed for mixtures with ϕ_w less than 0.5.

(b) Isothermally Crystallized Samples. Figure 5 shows the effect of crystallization temperature T_c on the observed melting temperature T_m* for PVF_2 and several of the PVF_2–PMMA mixtures; these effects are known to be due to morphological contributions such as the degree of perfection and the finite size of crystals.[16,18] A linear relationship is observed between T_c and T_m*. If we assume that the crystals are perfect and of finite size and that no recrystallization takes place during the melting run, the data in Figure 5 can be described by eq 1 for isothermal crystallization[16,18]

$$T_m^0 - T_m^* = \phi(T_m^0 - T_c) \quad (1)$$

where T_m^0 is the equilibrium melting point and ϕ is the stability parameter which depends on the crystal thickness. A least-squares fit of the data by eq 1 yields the values for T_m^0 and ϕ which are summarized in Table II. It may be noted that T_m^0 for pure PVF_2 is about 8.6°C higher than PVF_2 crystals in the 50:50 mixture. In addition, the degrees of melting temperature depression for the isothermally crystallized samples are comparable to that of the solution-cast samples.

In eq 1 where ϕ assumes the values between 0 and 1, ϕ = 0 implies $T_m^* = T_m^0$ for all T_c whereas ϕ = 1 implies $T_m^* = T_c$. Therefore, the crystals are most stable at ϕ = 0 and inherently unstable at ϕ = 1. In Table II the value for ϕ is about 0.2 for all compositions, suggesting that the crystals should be fairly stable. It is of interest to note that calorimetric measurements of other polymer crystals[16] also yielded comparable values for ϕ.

The last column of Table II lists the average endotherm areas, S (in arbitrary units), for the melting of PVF_2 crystals in the mixtures. If one assumes complete crystallization of the PVF_2 fraction which segregates from PMMA, the areas, S, for the mixtures should be 75, 61, and 45 since S = 90 for PVF_2 (cf. the first line of the last column). The close agreement between the estimated S and the actual data suggests that all crystallizable PVF_2 demixed from PMMA in the isothermal crystallization.

It has been reported recently that[19] the melting point of PVF_2 rises substantially upon annealing or isothermal crystallization at elevated temperatures because of the formation of crystalline form III in the polymer. This was not apparent in our test results as the crystals melted completely below 175°C and the x-ray study showed a prepon-

Table II
Analysis of Isothermal Crystallization Where T_m°, ϕ, and S are Equilibrium Melting Temperature, Stability Parameter of the Crystals, and Average Endotherm Area in Arbitrary Units, Respectively

	T_m°, °C	ϕ	S
PVF_2	173.8	0.198	90 ± 5
PVF_2–PMMA = 82.5:17.5	169.8	0.173	74 ± 5
PVF_2–PMMA = 67.5:32.5	168.5	0.175	60 ± 5
PVF_2–PMMA = 50:50	165.2	0.200	43 ± 3

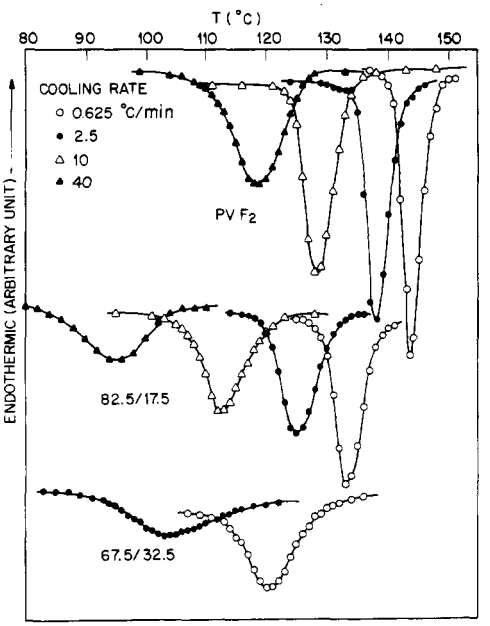

Figure 6. Thermograms of crystallization of PVF_2 in several mixtures under various cooling rates.

derance of crystals in form II. The difference probably arises from differences in the molecular weight and the head-to-tail arrangement of the polymeric materials used in the two studies.

(c) Crystallization and Melting Behavior Under Various Cooling and Heating Rates. Figure 6 displays several examples of thermograms for crystallization of PVF_2 under various cooling rates. There is a sharp drop in the crystallization temperature with the increases in the PMMA concentration and the cooling rate. In the entire range of cooling rates used in our study, the exothermic area did not change significantly with the cooling rate until the PVF_2 concentration fell below 67.5% and the cooling rate exceeded 5°C/min at which the crystallization behavior became difficult to observe. For example, there was no trace of crystallization for the sample PVF_2–PMMA = 60:40 when it was cooled down at a rate faster than 10°C/min.

The T_c and T_m for pure PVF_2 and the mixture PVF_2–PMMA = 67.5:32.5 are plotted in Figure 7 as functions of heating or cooling rate. More comprehensive results for the polymer system describing the dependence of T_c and T_m on the PVF_2 concentration at various heating or cooling rates are summarized in Figure 8. Here, T_c is defined as the temperature at which the exothermic curve peaks under a given cooling rate. As can be seen from Figures 7 and 8, there are large depressions in both the crystallization and the melting temperatures at each cooling or heating rate. In Figure 7, the increase of T_m for PVF_2 at higher heating rate may have been caused by superheating.

(d) Quenched Samples. Figure 9 shows the thermo-

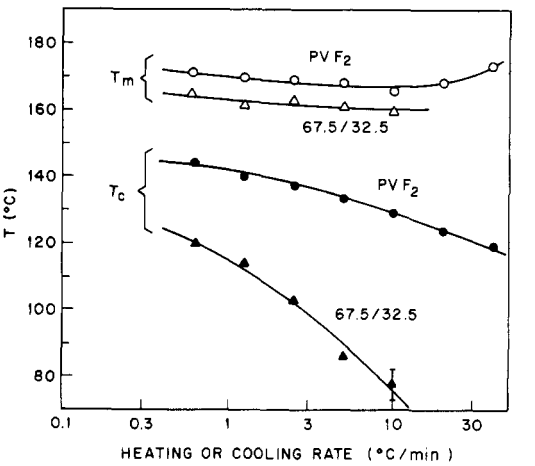

Figure 7. A plot of the melting and crystallization temperatures of PVF_2 crystals in pure PVF_2 and PVF_2–PMMA = 67.5:32.5 mixture vs. heating or cooling rate.

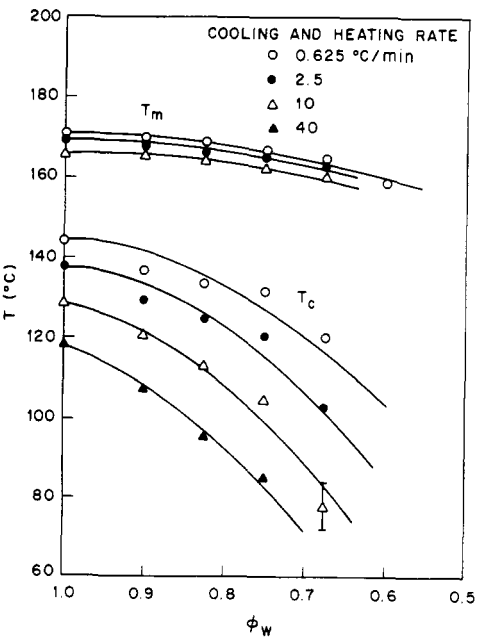

Figure 8. Dependence of melting and crystallization temperatures of the mixture on the weight fraction (ϕ_w) of PVF_2 and on the heating or cooling rate.

grams for the quenched samples of PVF_2, PMMA, and several mixtures obtained at the heating rate of 10°C/min. There is no indication of PVF_2 crystals in the 50:50 mixture but it has a glass transition temperature intermediate between that of PVF_2 (ca. −50°C)[5,20] and PMMA (ca. 90°C).

On the other hand, the mixture PVF_2–PMMA = 67.5:32.5 exhibits a glass transition at about 10°C, a crystallization temperature at about 70°C, and a melting point at about 160°C. Figure 10 summarizes the T_g, T_c, and T_m of the system as functions of the PVF_2 weight fraction ϕ_w. In the case of T_c, measurements at several heating rates are also included in the figure. It may be noted that our data for T_g are consistent with those of Noland et al.[5] for melt-mixed samples (also reproduced in Figure 10). The endotherm area for the melting of PVF_2 crystals in this experiment is shown in Figure 11. Again a substantial depression in the melting temperature is observed. Furthermore, there is no trace of crystallinity for the mixture with $\phi_w \leq 0.5$. In fact it was possible to obtain the mixture in an amorphous state at room temperature by quenching the mixture from

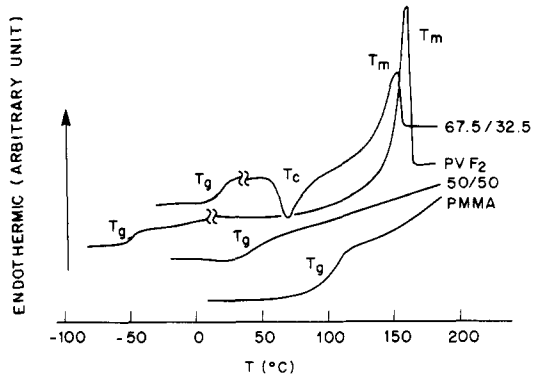

Figure 9. Thermograms of the quenched samples obtained at the heating rate of 10°C/min.

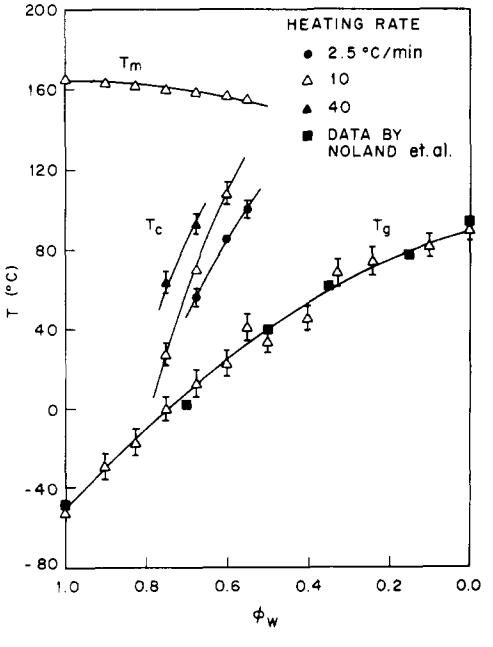

Figure 10. Dependence of glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) of the quenched mixture on the weight fraction (ϕ_w) of PVF_2.

the molten state with liquid nitrogen as long as $\phi_w \leq 0.7$.

Discussion

It is evident from examination of Figures 3, 5, 8, and 10 that both the thermal history of the sample and the temperature program employed in the experiment have important bearing on the general compatibility characteristics of the polymer–polymer system. In the quenching experiments described in program (d), for example, the two polymers seem to be compatible at temperatures above T_m and the quenched mixtures show intermediate glass transition temperatures between pure PVF_2 and PMMA. However, if these samples are slowly warmed to elevated temperatures or maintained for a period of time at temperatures below their melting points, PVF_2 starts to crystallize in the mixtures. Similarly, crystallization occurs when the mixture originally maintained at a temperature above T_m is slowly cooled to room temperature. In view of this strong dependence of the thermodynamic state of the mixture on temperature programs, it is convenient to discuss the test results by identifying programs (a) and (b) as "quasi-equilibrium" experiments and programs (c) and (d) as "kinetic" experiments. The word "kinetic" here refers to the kinetic aspect of heating or cooling.

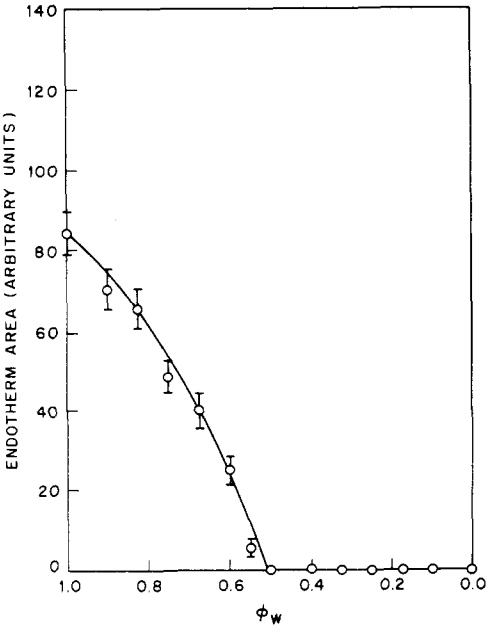

Figure 11. Dependence of the endotherm area due to the melting of PVF_2 crystals in the quenched mixture on the weight fraction (ϕ_w) of PVF_2.

Quasi-Equilibrium Experiments

Among the test results obtained in the quasi-equilibrium experiments, the most notable feature is perhaps the melting behavior of PVF_2 in the mixture which depends strongly upon the composition. The melting point depression, which is evident in our entire calorimetric study, intensifies progressively with the decrease in the PVF_2 content. This phenomenon bears close similarity to the melting point depression observed in the crystalline polymer–diluent systems. Several mechanisms have been proposed regarding the melting point depression in the latter systems.[18,21] For the PVF_2–PMMA system it has been suggested[6] that morphological effects such as size and perfection of the crystalline regions are responsible for the lowering of melting point. There are, however, at least two observations in our present study which cast some doubt on this mechanism as being the major cause. First, the isothermal crystallization experiments, program (b) (see Table II), show that the stability parameter ϕ, which is in fact a morphological parameter, is independent of composition. If the melting point depression is mainly due to morphological effects, ϕ should not be a constant and the straight lines in Figure 5 should have different slopes and extrapolate to a single equilibrium melting point. Second, in the study of the effects of heating rates on melting behavior of the mixture (see Figure 8), the melting point depression appears to be affected by the fraction of PMMA in the mixture but only very slightly by the heating rates. If morphological effects were significant, the melting behavior should be more susceptible to changes in the heating rate.

As an alternate explanation of the observed melting point depression phenomenon, the following considers the thermodynamic effects of mixing by extending the work on the crystalline polymer–diluent systems[18] to the crystalline polymer–amorphous polymer systems. This line of thought is prompted by the fact that amorphous mixtures obtained by quenching in liquid nitrogen exhibit compatible behavior.

The thermodynamic mixing of two polymers was treated by Scott[22] using the Flory–Huggins approximation.[21] For this system the chemical potential μ_{2u}^1 per mole of crystal-

lizable polymer units in the mixture relative to its chemical potential μ_{2u}^0 in the pure liquid can be expressed as

$$\mu_{2u}^1 - \mu_{2u}^0 = \frac{RTV_{2u}}{V_{1u}}\left[\frac{\ln V_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right) \times (1 - V_2) + \chi_{12}(1 - V_2)^2\right] \quad (2)$$

where, with the subscript 1 identified with the amorphous polymer and 2 with the crystalline polymer, V is the volume fraction, V_u is the molar volume of the repeating units, m is essentially the degree of polymerization.[22] Also χ_{12} is the polymer–polymer interaction parameter, R is the gas constant, and T is the absolute temperature.

The difference in the chemical potential between a crystalline polymer unit μ_{2u}^c and the same unit in the pure liquid state μ_{2u}^0 can be written as,

$$\mu_{2u}^c - \mu_{2u}^0 = -(\Delta H_{2u} - T\Delta S_{2u}) = -\Delta H_{2u}(1 - (T/T_m^0)) \quad (3)$$

where ΔH_{2u} and ΔS_{2u} are the enthalpy and entropy of fusion per mole of repeating unit and the ratio $\Delta H_{2u}/\Delta S_{2u}$ is assumed to be independent of temperature and equal to T_m^0, the equilibrium melting temperature.

On the condition that at the melting point T_m of the mixture the chemical potentials of the crystalline component in the crystalline and liquid phases should be identical[21] one obtains from eq 2 and 3

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_{2u}}{\Delta H_{2u}V_{1u}}\left[\frac{\ln V_2}{m_2} + \left(\frac{1}{m_2} - \frac{1}{m_1}\right) \times (1 - V_2) + \chi_{12}(1 - V_2)^2\right] \quad (4)$$

For the problem at hand, both m_1 and m_2 are very large compared with 1; eq 4 therefore reduces to

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_{2u}}{\Delta H_{2u}V_{1u}}\chi_{12}(1 - V_2)^2 \quad (5)$$

Equation 5 therefore describes the melting point depression due to mixing of a crystalline polymer and an amorphous polymer. We note in passing that eq 4 reduces to the familiar expression for the melting point depression of polymer–diluent systems if we let $m_1 = 1$ and $m_2 \to \infty$.

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{RV_{2u}}{\Delta H_{2u}V_{1u}}[(1 - V_2) - \chi_{12}(1 - V_2)^2] \quad (6)$$

There are two points of interest on inspection of eq 5. First, unlike the case in the polymer–diluent systems, the interaction parameter χ_{12} plays a decisive role on the melting behavior of the crystalline polymer–amorphous polymer systems. Thus the depression of melting point can be realized only if χ_{12} is negative. On the other hand if χ_{12} is positive as in most cases, the melting point should rise above the equilibrium melting temperature. This is an interesting point which calls for experimental verification. Second, since χ_{12} and ΔH_{2u} enter eq 5 in the form of a ratio it is no longer possible to deduce these two quantities simultaneously from the calorimetric measurements, a feat that is feasible in the case of polymer–diluent systems (cf. eq 6).

The fact that the depression of the melting point can be realized only if χ_{12} is negative is in keeping with the Scott's condition for the miscibility of the two polymers,[22]

$$\chi_{12} \leqq \frac{1}{2}\left[\frac{1}{m_1^{1/2}} + \frac{1}{m_2^{1/2}}\right]^2 \quad (7)$$

which requires χ_{12} to be near zero or negative for the polymer pair whose m_1 and m_2 are much greater than 1.

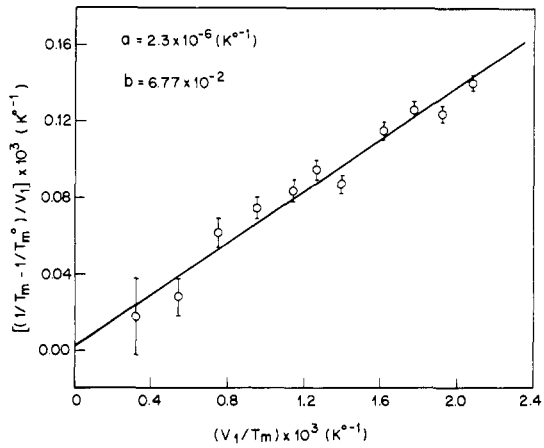

Figure 12. A plot of the quantity $(1/T_m - 1/T_m^0)/V_1$ against V_1/T_m for the PVF_2–PMMA system where T_m is the melting point of PVF_2 crystals in the mixture, T_m^0 is the melting point of pure PVF_2, and V_1 is the volume fraction of PMMA in the mixture.

Returning to eq 5, we assume χ_{12} to be of the following form by neglecting the effects of entropy[22] and V_2,[23]

$$\chi_{12} = BV_{1u}/RT \quad (8)$$

where B is the interaction energy density characteristic of the polymer pair. Substitution of eq 8 into eq 5 yields a linear relationship between $(1/V_1)[(1/T_m) - (1/T_m^0)]$ and V_1/T_m,

$$\frac{1}{V_1}\left[\frac{1}{T_m} - \frac{1}{T_m^0}\right] = -\frac{BV_{2u}}{\Delta H_{2u}}\frac{V_1}{T_m} \quad (9)$$

In Figure 12, the data obtained in Figure 3 are replotted using $(1/V_1)[(1/T_m) - (1/T_m^0)]$ and (V_1/T_m) as variables. A least-squares fit of the data yields a straight line intersecting the vertical axis near zero. Calculation shows a value, a, of $2.3 \times 10^{-6}K^{-1}$ for the ordinate of the intersection point and 6.77×10^{-2} for the slope b. In view of the extremely small a, the use of the expression in eq 8 would appear justified. Using the data $V_{1u} = 84.9$ cm³/mol, $V_{2u} = 36.4$ cm³/mol,[24] $\Delta H_{2u} = 1.6$ kcal/mol,[25] $\rho_1 = 1.20$ g/cm³, and $\rho_2 = 1.80$ g/cm³, where ρ is the density, we find from the value for the slope b,

$$B = -2.98 \text{ cal/(cm}^3 \text{ of PMMA)}$$

$$\chi_{12} = -0.295 \text{ at } 160°C$$

The negativeness of χ_{12} for the PVF_2–PMMA system indicates that the polymer pair can form a thermodynamically stable compatible mixture at temperatures above the melting point defined by eq 5. In addition the magnitude of the χ_{12} value appears to be quite reasonable in comparison with data obtained for other compatible polymer–polymer mixtures.[26-28]

We have therefore demonstrated that the melting point depression of PVF_2 crystals in the PVF_2–PMMA system can be accounted for by Scott's thermodynamic treatment of mixing between two polymers. Furthermore, provided the quantity ΔH_{2u} can be independently obtained, Scott's equation permits a direct determination of the interaction parameter between a crystallizable polymer and an amorphous polymer.

The foregoing discussion has been based on the assumption that the two polymers are miscible in the molten state. Although the negativeness of χ_{12} is itself a sufficient proof of miscibility, as mentioned before, supporting evidence is also found in the depression of the crystallization tempera-

ture T_c (Figures 7 and 8) and in the single T_g of the mixture quenched from a temperature above T_m. (In Figure 10, the majority of the quenched mixtures except those with ϕ_w near 1 are in the amorphous state.)

"Kinetic" Experiments. The cooling runs of the temperature program depicted in Figure 1c can be thought of as representing the thermal history of PVF_2 and PMMA being mixed in the melt and cooled down to room temperature. As shown in Figures 7 and 8 the crystallization behavior of the mixture depends strongly upon the PVF_2 concentrations and the cooling rate. At higher PVF_2 concentrations ($\phi_w > 0.6$) the crystallization temperature falls progressively with the increase in the cooling rate and the decrease in ϕ_w. At ϕ_w below 0.6, however, it becomes difficult to detect the crystallization exotherm in the sample. In fact, at ϕ_w below 0.55 it is possible to obtain the mixture in the amorphous state at room temperature using a cooling rate as low as 0.625°C/min. The amorphous mixtures are obviously metastable or at least nearly metastable at room temperature and can be rendered stable or nearly stable (upon crystallization of PVF_2) by proper heat treatment at temperatures between T_m defined by eq 5 and T_g obtained in Figure 10. For example, as shown in Figure 5 it was possible to make PVF_2 in an amorphous 50:50 mixture crystallize between 95 and 120°C. Also, in a brief study, crystallization was observed in an amorphous PVF_2–PMMA = 40:60 sample after exposure to 85°C for 65 hr.

As with the polymer–diluent system, the depression of crystallization temperature in the mixture may be ascribed to several factors,[18] and these effects are likely to be more pronounced here because of the high molecular weight of the amorphous polymer and the attendant rise in its viscosity. First, as crystallization proceeds, there is a reduction of crystallizable polymer in the melt and hence a concomitant decrease in the thermodynamic driving force favoring crystallization. Second, as PVF_2 is diluted more with PMMA, the transport process of PVF_2 segments to the crystallite–melt interface becomes more protracted, causing retardation in the rates of nucleation and growth. Third, the T_g of the mixture rises with the increase in the PMMA content which delays the diffusion of PVF_2 segments in the melt. Finally, as T_m is depressed more with the increase in the PMMA content, the dwell time of the mixture in the temperature gap between T_m and T_g decreases in a cooling run. This tends to limit further the migration of the crystallizable polymer. The above discussion is based on the obvious assumption that the system is compatible in the molten state.

Examining again the results in Figure 10, any sample with ϕ_w less than 0.3 will probably require a very long time to develop crystals at room temperature since the mixture will have a T_g higher than 65°C and a melting point depression of more than 20°C. In effect, these samples ($\phi_w < 0.3$) are in a metastable state and therefore it may be less satisfactory to use the rule of additivity or the Gordon–Taylor expression for the T_g of the mixture to measure the compatibility of the polymer system[5,10] without taking into proper account the kinetic effect of cooling.

Conclusions

Calorimetric studies were carried out on DMF solution cast PVF_2–PMMA mixtures to measure the glass transition, melting, and crystallization behavior of the system under several thermal programs. Results from quasi-equilibrium experiments indicate that the polymer pair is compatible in the molten state but develops PVF_2 crystals on cooling from melt. The melting temperature of the crystallized mixture drops considerably with the increase in the PMMA content. To describe this phenomenon, an expression appropriate to the crystalline polymer–amorphous polymer system is derived from Scott's equation for thermodynamic mixing of two polymers and applied to the test data. Good agreement is attained between analytical results and the observed melting point depression. In addition the analysis yields a value of −0.295 at 160°C for the interaction parameter χ_{12} between PVF_2 and PMMA. The magnitude of χ_{12} compares reasonably with those measured for other compatible polymer–polymer systems.

The crystallization behavior of PVF_2 in the mixture is found to be significantly affected by the cooling rate and the composition of the mixture. The crystallization temperature decreases progressively with the increase in the cooling rate and the PMMA content. Both factors are believed to be attributable to the ability of PVF_2 segments to migrate and to the change of composition in the melt during crystallization. Thus, with the range of cooling rates used in the study, it is possible to suppress crystal transformation in the mixture when $\phi_w \leq 0.5$. Finally, it is pointed out that because of the strong kinetic effects due to cooling on the thermodynamic state of the mixture, adequate consideration should be given to the effects of cooling rate on the state of the mixture when applying the rule of additivity or the Gordon–Taylor equation to study the compatibility of the crystalline polymer–amorphous polymer pairs.

Acknowledgment. We are grateful to Drs. T. K. Kwei and E. Helfand for valuable discussions. We are also grateful to Mr. F. J. Padden, Jr., for the x-ray diffraction analysis and Mrs. M. Y. Hellman for the polymer characterization.

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