retain the 0°, ±120° backbone rotational states in all calculations reported here. Rotational state statistical weights[23,47] $\eta = 0.8 \exp(200/T)$, $\tau = 0.5$, and $\omega = \omega' = \omega'' = 1.5 \exp(-1000/T)$ were used at $T = 150$ °C for the calculations performed on PS, PPMS, PPCS, PS-PPCS, and PPMS-PPCS.

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(51) Dr. E. Saiz has studied the relation between variations in the RIS model and the calculated molar Kerr constants for PPCS. He finds, as Nagai and Ishikawa[34] did, that the magnitude of the calculated molar Kerr constants for PPCS is sensitive to the details (rotational state energies, chain geometry, etc.) of the RIS model employed and cautions that Kerr constants may only be useful in the characterization of those polymers whose RIS models are firmly established.

Ternary Polymer Mixtures

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ABSTRACT: Two incompatible polymers, poly(methyl methacrylate) and poly(ethyl methacrylate), can be brought together by poly(vinylidene fluoride) to form ternary mixtures which are compatible. The melting point depression of PVF_2 in the ternary system can be calculated from Scott's equation. Mixtures containing 40 to 70% by weight of PVF_2 are amorphous when quenched from melt and each mixture consists of a single phase whose T_g is equal to the volume fraction average of the T_g of component polymers.

In previous studies[2,3] of mixtures of poly(vinylidene fluoride) (PVF_2) with poly(methyl methacrylate) (PMMA) or poly(ethyl methacrylate) (PEMA), binary interaction parameters obtained from melting point depression of PVF_2 were found to be negative, indicative of compatibility in the molten state. When quenched from the melt, blends of PVF_2 with PMMA were amorphous and exhibited a single glass transition for each composition.[2,4,5] Quenched mixtures containing 60% or more PEMA were also amorphous and showed single glass transitions. When the PEMA content is low, crystallization of PVF_2 was observed even at high quenching rates (≥320 °C/min) and the crystalline regions coexisted with two conjugated amorphous phases which contained ~100 and ~45 wt % PVF_2.[3]

Although both PMMA and PEMA are compatible with PVF_2 and the binary interaction parameters are similar in magnitude, the two methacrylate polymers are incompatible with each other.[6] Therefore we wish to explore the possibility of rendering these two polymers compatible using PVF_2 as a common solvent. The notion of bringing together two incompatible polymers by a third material is practiced with low molecular weight polymers in coating formulations but, to our knowledge, has not been demonstrated with high molecular weight vinyl polymers.

The principal tool of our investigation is calorimetry. The melting temperatures of PVF_2 in the as-cast films of ternary mixtures and the glass transition temperatures of quenched specimens were determined. Electron microscope studies of PMMA–PEMA blends were also undertaken to verify the results of calorimetric investigations.

Experimental Section

Materials. Poly(vinylidene fluoride), Kynar 821, from Pennwalt Corp., poly(methacrylate), Acrylite H-12, from American Cyanamid Co., and poly(ethyl methacrylate) from Haven Chemicals Inc. were the same materials as used in earlier studies.[1,3] Films were cast from 3% dimethylformamide (DMF) solution and maintained at 90 °C in a forced-air oven for 3 days. To ensure complete removal of DMF from films containing high percentages of PMMA, all films were given additional drying at 130 °C in a vacuum oven overnight. The compositions of mixtures are recorded in weight percentages unless otherwise stated.

Calorimetry. Calorimetric studies were conducted using a Du Pont Thermal Analyzer, Model 990, with a DSC cell. Melting point measurements were carried out at a heating rate of 10 °C/min. In the determination of glass transitions, the specimens were quenched from the melt at 50 °C/min to −120 °C and then heated at 20 °C/min. The endothermic response associated with glass transition was often broad and weak in ternary mixtures and triplicate runs were made in most cases to ascertain T_g. The uncertainty in T_g measurement is ±2 °C.

Electron Microscopy. Kato's technique of OsO_4 staining[7] was applied to PMMA–PEMA mixtures. Ultrathin sections of stained specimens were examined with transmission electron microscopy.

Results and Discussions

(1) PMMA–PEMA Mixtures. Although PMMA and PEMA are chemical homologues, phase separation has been reported to take place in chloroform solution.[6] Because the refractive index difference between the two polymers is insignificant, the transparency of films cast from DMF cannot be taken as an indication of homogeneous mixing. Rather, evidence for the two-phase nature of these films is seen in calorimetric results. The thermograms of PEMA, PMMA, and four mixtures containing 85, 60, 40, and 15% PEMA, respectively, are shown in Figure 1. Each of the four mixtures exhibits two glass transitions at 68 and 104 °C, nearly identical with the T_g values for the pure polymers, namely, 67 °C for PEMA and 102 °C for PMMA. The magnitudes of ΔC_p associated with the two transitions in curves B to E agree well with the predictions based on the ΔC_p values of the component polymers and the compositions of the mixtures (Figure 2). These results suggest very strongly that PMMA–PEMA mixtures undergo phase separation into nearly pure components.

Further evidence for the two-phase nature of the blends was obtained from electron microscopy. Although we did not anticipate preferential absorption of osmium tetraoxide in either polymer, the staining technique revealed vividly the presence of microscopic domains. Typical photomicrographs are shown in Figures 3A and 3B. Judging both from the cutting mark left by the diamond knife on the hard phase and from phase volume, we believe that the spherical domains consist of PMMA.

(2) Melting Point Depression of PVF_2 in Ternary Systems. The melting temperatures of PVF_2 in ternary mixtures are listed in Table I. The value of melting point depression, ΔT_m, at constant PVF_2 content is insensitive to the ratio of two methacrylate polymers because the binary in-

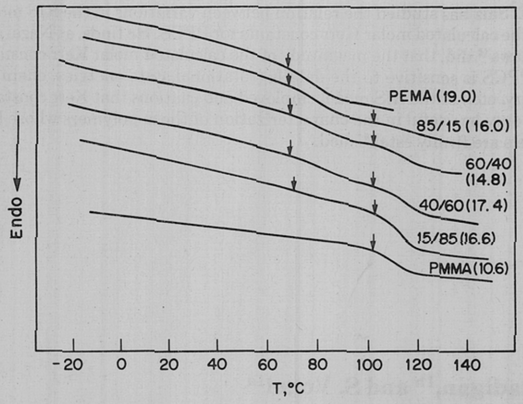

Figure 1. Thermograms of PEMA, PMMA, and their mixtures. (Number in parentheses indicates weight in milligrams.)

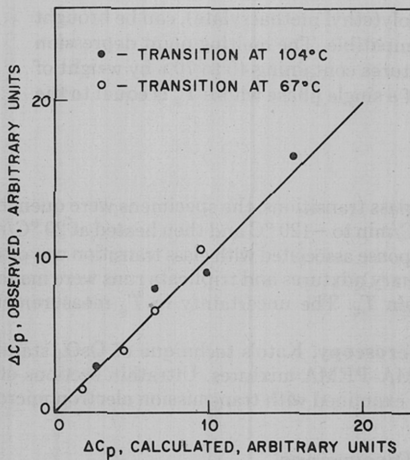

Figure 2. ΔC_p values for the transitions of PMMA–PEMA mixtures.

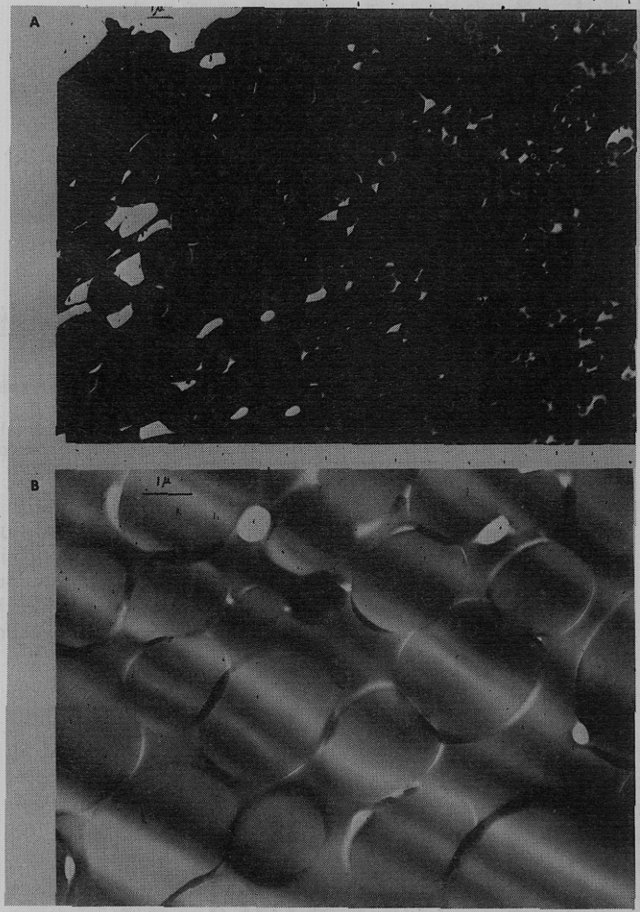

Figure 3. Electron microscope photographs of PMMA–PEMA blends: (top) PMMA/PEMA = 40/60; (bottom) PMMA/PEMA = 85/15, also visible in optical microscope at 400×.

teraction parameters for PVF_2–PEMA pairs are similar in magnitude.

As in the case of binary polymer mixtures, the melting point depression in a ternary system can be derived readily from existing equations. Throughout the following discussion, we designated PMMA, PVF_2, and PEMA as components 1, 2, and 3, respectively. The chemical potential of component 2 in a ternary mixture is given by Scott's equation,[8]

$$(\mu_2 - \mu_2{}^0)/RT = \ln \phi_2 + (1 - \phi_2) - \phi_2 m_2/m_1 - \phi_3 m_2/m_3 + (\chi_{21}\phi_1 + \chi_{23}\phi_3)(1 - \phi_2) - \chi_{13}\phi_1\phi_3 m_2/m_1 \quad (1)$$

In eq 1, ϕ is the volume fraction, m is the number of segments, and the χ's are Flory's interaction parameters[9] with the attendant relationships shown in eq 2 and 3,

$$\chi_{ij}/m_i = \chi_{ji}/m_j \quad (2)$$

and

$$\chi_{ij} = B_{ij}\overline{V}_i/RT \quad (3)$$

where $\overline{V}_i$ is the molar volume of chain i. We note that in the lattice theory the segments are chosen to be of equal volume and the m's are defined in relative terms. Since component 2 is the one of concern, we express $m_1 = \overline{V}_1/\overline{V}_{2u}$ and $m_3 = \overline{V}_3/\overline{V}_{2u}$ where $\overline{V}_{2u}$ is the molar volume of the repeating unit of component 2. Combination of eq 1 and 3 then results in the following when m_2 is large:

$$\Delta\mu_2/m_2 = \overline{V}_{2u}[(B_{12}\phi_1 + B_{32}\phi_3)(1 - \phi_2) - B_{13}\phi_1\phi_3] \quad (4)$$

When $\Delta\mu_2/m_2$ is equated to the difference in chemical potential between a crystalline polymer unit and the same unit in the pure liquid state, we obtain eq 5 which relates T_m to composition, binary interaction constants, and heat of fusion per unit, ΔH_{2u},

$$(1 - T_m/T_m{}^0) = -\frac{\overline{V}_{2u}}{\Delta H_{2u}} \times [(B_{12}\phi_1 + B_{32}\phi_3)(1 - \phi_2) - B_{13}\phi_1\phi_3] \quad (5)$$

All parameters on the right-hand side of eq 5, except B_{13}, are known from previous studies ($\overline{V}_{2u} = 36.4$ cm³/mol, $\Delta H_{2u} = 1.6$ kcal/mol, $B_{12} = -2.98$, $B_{32} = -2.86$). A plot of $\Delta T_m/T_m{}^0$ vs. $-(B_{12}\phi_1 + B_{32}\phi_3)(1 - \phi_2)$ therefore allows us to assess the applicability of eq 5 and the contribution of B_{13}. In Figure 4, the line drawn through the origin with a slope of $\overline{V}_{2u}/\Delta H_{2u}$ fits experimental data very well and indicates that the value of B_{13} is approximately zero (±0.5). The excellent agreement between theory and experiment suggests that the ternary system is compatible at elevated temperatures. (Samples 2 and 3 are exceptions for reasons to be discussed later.)

The parameter B_{13} is a measure of the interaction between two methacrylate polymers. Unfortunately, it is difficult to ascertain the exact magnitude of B_{13} in the present method because the term $B_{13}\phi_1\phi_3$ is the small difference between two large numbers. But B_{13} is most likely positive in sign because the two methacrylate polymers are immiscible. The magnitude of B_{13} can be quite small because the critical value of B_{13} is estimated from molecular weight considerations[8] to be only about 0.025.

(3) Glass Transitions. In this section we make use of T_g

Table I
Melting and Glass Transition Temperatures of Ternary Mixtures

Sample	Composition, wt %			ΔT_m, °C	Quenched samples	
	PVF_2	PMMA	PEMA		T_g, °C	Remarks
1	20	60	20		27, 96	Amorphous
2	30	10.5	59.5	11.1[a]	39, 86	Amorphous
3	30	42	28	9.1[a]	29, 86	Amorphous
4	30	59.5	10.5	18.6	62	Amorphous
5	40	15	45	14.1	37	Amorphous
6	40	30	30	14.1	40	Amorphous
7	40	45	15	13.8	48	Amorphous
8	50	7.5	42.5	10.4	22	Amorphous
9	50	30	20	10.1	30	Amorphous
10	50	42.5	7.5	10.8	37	Amorphous
11	60	10	30	8.1	10	Amorphous
12	60	20	20	7.2	15	Amorphous
13	60	30	10	6.1	20	Amorphous
14	70	4.5	25.5	4.6	31[b]	Crystalline
15	70	18	12	4.7	2	Amorphous[c,d]
16	70	25.5	4.5	5.6	6	Amorphous[c,e]
17	80	3	17	1.6	−54, 20 (?) 88 (?)	Crystalline
18	80	12	8	1.7	−54, 20 (?) 88 (?)	Crystalline
19	80	17	3	1.6	−54, 20 (?) 88 (?)	Crystalline

[a] Not included in Figure 4. [b] Not included in Figure 5. [c] Crystallization exotherm approximately equal to melting endotherm; sample essentially amorphous in the quenched state. [d] Crystallize at 40 °C. [e] Crystallize at 50 °C.

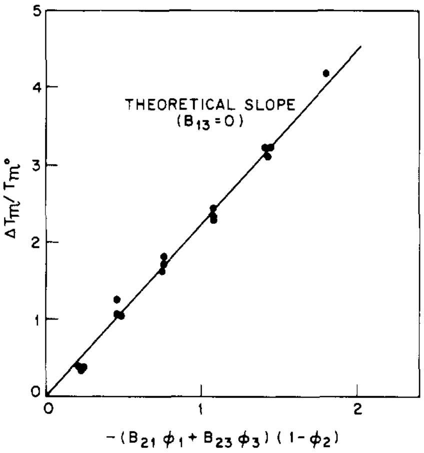

Figure 4. Melting point depression of PVF_2 in ternary system.

measurements to deduce phase structures in ternary blends. Because two of the components are incomptible and the third one is crystallizable, phase structures are exceedingly complex and meaningful results can be obtained only under selective conditions. Samples quenched from the molten state at 50 °C/min appear to be well suited for the T_g study because crystallization of PVF_2 is suppressed in most cases and the identification of T_g is free from the ambiguity arising from the small endothermic event seen at ~40 °C in slow-cooled PVF_2 films.[3] The analysis of T_g data is further aided by the finding that the T_g of PVF_2-PMMA or PVF_2-PEMA mixtures can be expressed simply as the volume fraction average of the T_g of the component polymers (Figure 5). This relation, which had escaped our notice earlier, is a natural consequence of the Bueche-Kelley equation[10] derived from the assumption of additivity of free volumes,

$$T_g = (\phi_1 T_{g1} + k\phi_2 T_{g2})/(\phi_1 + k\phi_2) \qquad (6)$$

where k is the ratio of thermal expansion coefficients $\Delta\alpha_2/\Delta\alpha_1$, with $\Delta\alpha = \alpha(\text{liquid}) - \alpha(\text{glass})$. (Alternate derivation based on additivity of configurational entropies will result in an equation of similar form but different meaning of k.) Apparently the value of k is unity for PVF_2–methacrylate polymers.

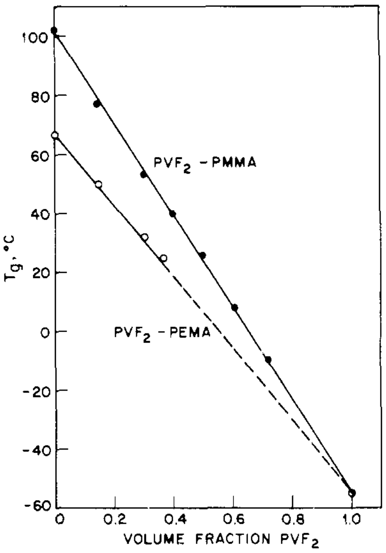

Figure 5. Glass transition temperature of binary PVF_2-poly(methacrylate) mixtures. Dotted line represents regions of two glass transitions.

When samples are arranged in the order of increasing PVF_2 content, a trend in T_g data emerges. When the amount of PVF_2 is low, about 30% or less, two T_g's are detected (samples 1 to 3). At higher PVF_2 content, up to about 70%, a single T_g is found for each mixture. Finally, when the blend contains 80% PVF_2, crystallization persists and multiple transitions are again observed. Each category will be discussed separately.

When PVF_2 is a minor component in the ternary blend, it may distribute itself in the two poly(methacrylate) phases. One would then expect the coexistence of a PMMA-PVF_2 phase with a PEMA-PVF_2 phase. This appears to be the case for samples 1, 2, and 3. One T_g is lower than that of PEMA and the other is lower than that of PMMA. The composition of each phase can be estimated from its T_g (Figure 5) and compared with the overall composition of the blend for proper material balance. The calculated values given in Table II substantiate the validity of the above model. It is noticed,

Table II
Phase Compositions in Ternary Blends[a]

	Ternary blend			Phase A		Phase B		Total PVF_2,
Sample	PVF_2	PMMA	PEMA	PVF_2	PEMA	PVF_2	PMMA	Calcd
1	20	60	20	15.8 (0.330)	20	3.8 (0.040)	60	19.6
2	30	10.5	59.5	28.6 (0.230)	59.5	1.8 (0.105)	10.5	30.4
3	30	42	28	20.7 (0.315)	28	7.4 (0.105)	42	28.2

[a] Value in parentheses indicates volume fraction.

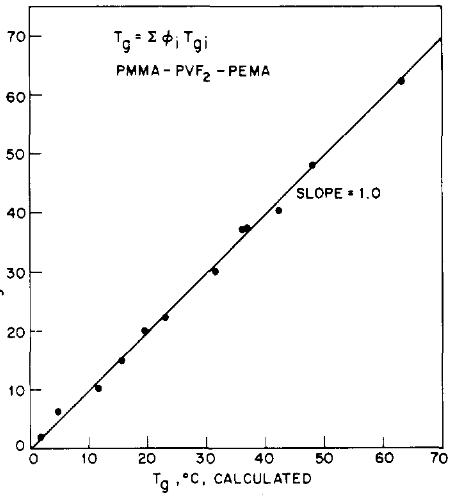

Figure 6. Glass transition temperatures of ternary mixtures.

however, that the calculated phase compositions most likely do not represent equilibrium values because the compositions of phase B in samples 2 and 3 are identical but the compositions of phase A are not.

The two-phase nature of samples 2 and 3 apparently contributes to the anomalously low ΔT_m values which are not included in Figure 4. As the amount of PMMA increases in this series, there is an improvement in compatibility. Only one T_g is manifested by sample 4 and the ΔT_m value obeys eq 5.

Each of the samples from 4 through 16, containing 40 to 70% PVF_2, exhibits a single T_g. However, the thermograms of samples 14, 15, and 16 have additional features. A large melting endotherm, indicative of crystallized PVF_2, is prominent in the thermogram of sample 14 (PVF_2/PMMA/PEMA 70/4.5/25.5). Sample 15 which contains a higher percentage of PMMA undergoes crystallization at 40 °C during the thermal scan but the area of crystallization exotherm is comparable to the area of subsequent melting endotherm. Sample 16 behaves similarly. We consider both samples as essentially amorphous in the quenched state.

The glass transition temperatures of these amorphous, single-phase samples (4 through 13, 15 and 16) are now compared with eq 7.

$$T_g = \textstyle\sum_i \phi_i T_{gi} \qquad (7)$$

The agreement between the experimental and calculated values is gratifying (Figure 6). The role of PVF_2 in rendering the two methacrylate polymers miscible is thereby demonstrated. The implication of eq 7 with regard to the additivity of free volumes suggests extensive mixing of the different segments but the nature of segmental interaction remains to be explored.

When the PVF_2 content is further increased to 80%, the quenched samples are highly crystalline. The glass transition at −54 °C is obviously due to PVF_2. Two additional transitions at 20 and 88 °C, respectively, appear to exist but they are very weak probably because only minor quantities of PMMA and PEMA are present in these films. We made no attempt to estimate the compositions of the various phases in these materials.

Conclusion

Poly(methyl methacrylate), poly(ethyl methacrylate), and poly(vinylidene fluoride) form compatible mixtures over a wide range of compositions. The lowering of the melting point of PVF_2 in the ternary blends can be calculated from Scott's equation for the chemical potential of a polymer in a three-component system.

When the PVF_2 content is less than 30%, it is distributed in two amorphous phases, namely, PMMA-PVF_2 and PEMA-PVF_2. Mixtures containing 40 to 70% PVF_2 are also amorphous but each mixture consists of a single phase whose T_g is equal to the volume fraction average of the T_g of component polymers. As the amount of PVF_2 is further increased to 80%, the mixture appears to contain crystalline regions as well as multiple amorphous phases.

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