37.5% MLEX. Above this composition, other forces, which appear to be composition independent, control T_g. It appears from these data that chain conformations control the glass transition activation energies at low MLEX loadings, and that these forces are reduced, or eliminated, at high MLEX concentrations.

In Summary. The dielectric relaxations of solid solutions of bisphenol A–diphenyl carbonate (MLEX)/Lexan polycarbonate (BPAPC) have been studied as a function of composition. The T_g of the solutions is a continuous function of composition indicating no loss of "excess" free volume upon the addition of the MLEX to BPAPC. The T_g data have been interpreted in terms of a free volume additivity equation used to explain many polymer/diluent systems. Although a single relaxation distribution is observed for the glass transition, indicating possible correlated polymer/small molecule motions, the data can be interpretated in terms of a molar averaging of the individual relaxations occurring at identical temperatures. The T_g's are Arrhenius activated and exhibit composition independence above 50 vol % MLEX. Below this value the apparent activation energies exhibit plasticization effects. The activation energies indicate that MLEX has a greater effect on the energies involved in the BPAPC reorientations at T_g than vice versa. This effect is explained in terms of the removal of localized motion in the polymer and its effect on intra- and interchain interactions as well as polymer–molecule interactions.

The sub-T_g relaxations reflect the T_g relaxation analysis. MLEX and BPAPC exhibit similar molecular relaxations: $T_g(\alpha)$, combined phenyl ring carbonyl motion (β), and carbonyl motion (γ). The addition of MLEX to BPAPC or BPAPC to MLEX causes the β relaxation to disappear and at intermediate compositions the relaxations appear to be a molar averaging of the γ relaxations of the pure components and are thus uncorrelated. The activation energies for these relaxations reflect this behavior.

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Pyroelectricity in Polymer Blends of Poly(vinylidene fluoride)

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ABSTRACT: Polymer blends of poly(vinylidene fluoride) with both poly(methyl methacrylate) and poly(vinyl fluoride) were prepared and evaluated for pyroelectric activity. Percent crystallinity and extent of α, β, γ, and amorphous phases were evaluated by both x-ray diffraction and infrared spectroscopy. The correlations observed are supportive of a dipole-reorientation model for pyroelectricity.

Pyro- and piezoelectricity in poly(vinylidene fluoride) (PVF_2) are thought to be due to the existence of an oriented dipolar structure induced by "poling" polymer films in a high dc field ("dipole-reorientation" model),[1–5] or to the existence of a nonhomogeneous space charge distribution ("space-charge" model),[6–10] or both phenomena superimposed.[11,12] The purpose of this study was to vary the crystallinity and phases of PVF_2 by blending it with poly(vinyl fluoride) (PVF) and poly(methyl methacrylate) (PMMA) and attempt to correlate pyroelectric behavior with the extent of crystalline phase present. If such a correlation exists, it would be hard to rationalize it in terms of a space-charge model, i.e., further credence would be added to the dipole-reorientation model.

Morphological studies[13–19] have shown that there are three crystalline forms of PVF_2. The α form (form II) has the trans-gauche-trans-gauche′ configuration[16] and the β form (form I) has the planar zigzag conformation.[19] The structure of the γ form (form III) is not established. However, there are

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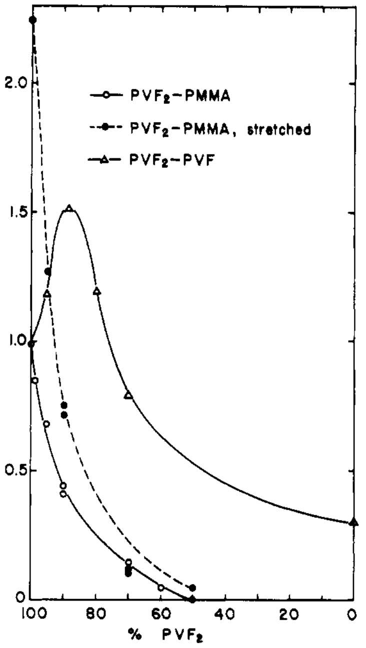

Figure 1. Change in pyroelectric coefficients of polymer blends with change in their composition.

some reports[13,17,20] claiming that the γ form is very similar to the β form. The $-CF_2-$ group of the monomer unit has a dipole moment of 2.1 D.[4] The β form contains two parallel chains and two monomer units per unit cell[19] with a net polarization of 1.3×10^5 C cm^{-2}.[4] The α form contains two antiparallel chains and four monomer units[6] per unit cell. The average dipole moment per monomer unit in the individual α chains is approximately half of that in the β chains, but the net polarization in the α phase is zero due to the antiparallelism of the chains.

The fraction of the planar zigzag form can be increased (about 50%) by stretching the film,[19,21,22] by crystallization from dimethyl sulfoxide solution,[23] or by crystallization from the melt under high pressure.[15,21] The crystallinity of PVF$_2$ can also be changed by making blends with other polymers. PMMA is compatible with PVF$_2$ and the crystallinity of PVF$_2$ in this mixture decreases as the fraction of PMMA increases.[24,25] On the other hand, blending with PVF increases the crystallinity of PVF$_2$, especially of the planar zigzag forms.[26]

Experimental Section

Films of polymer blends were cast from hot solutions of the blends in *N,N*-dimethylformamide (DMF). The concentrations were approximately 15% for PVF$_2$/PMMA blends and 3-15% for PVF$_2$/PVF blends. Number average molecular weights of PVF$_2$, PVF, and PMMA were 120 000, 87 500, and 24 250, respectively. In forming a film, the solution was first spread uniformly on a glass plate using a Gardner Ultra Applicator and dried in an air oven at 110 °C for 30 min. This was followed by subsequent heating at 200 °C for approximately 30 min, which reduced the roughness of the surface. Such an annealing procedure was found necessary to prevent electrical breakdown during subsequent poling. The thickness of the films obtained was typically 20-25 μm for PVF$_2$/PMMA and 5-15 μm for PVF$_2$/PVF. Nichrome electrodes of 1.26 cm^2 area were vacuum evaporated onto both sides of the films, and electrical leads were attached to the electrodes using conducting epoxy adhesive (Acme

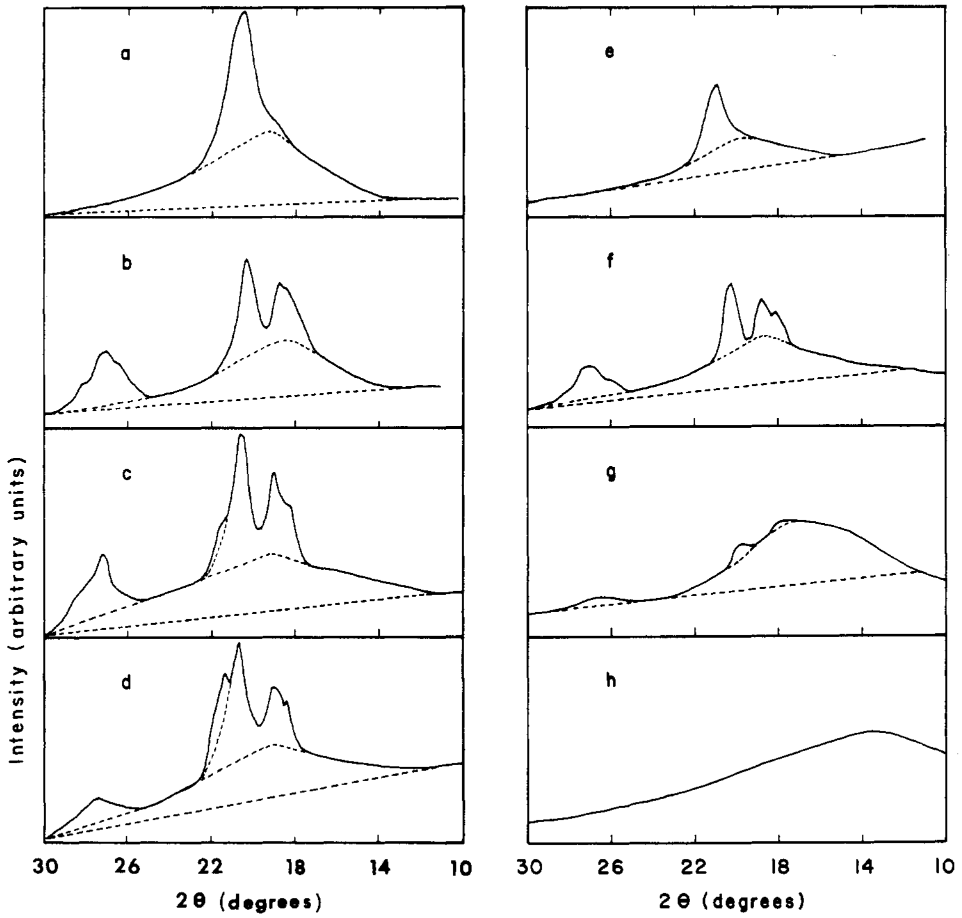

Figure 2. X-ray diffraction intensity patterns of the polymer films: (a) β-PVF$_2$; (b) PVF$_2$; (c) PVF$_2$/PVF (88.5-11.5%); (d) PVF$_2$/PVF (70-30%); (e) PVF; (f) PVF$_2$/PMMA (90-10%); (g) PVF$_2$/PMMA (50-50%); (h) PMMA. All films were heated at 200 °C for 30 min after casting from DMF solutions, with the exception of (a) which was crystallized from dimethyl sulfoxide solution.

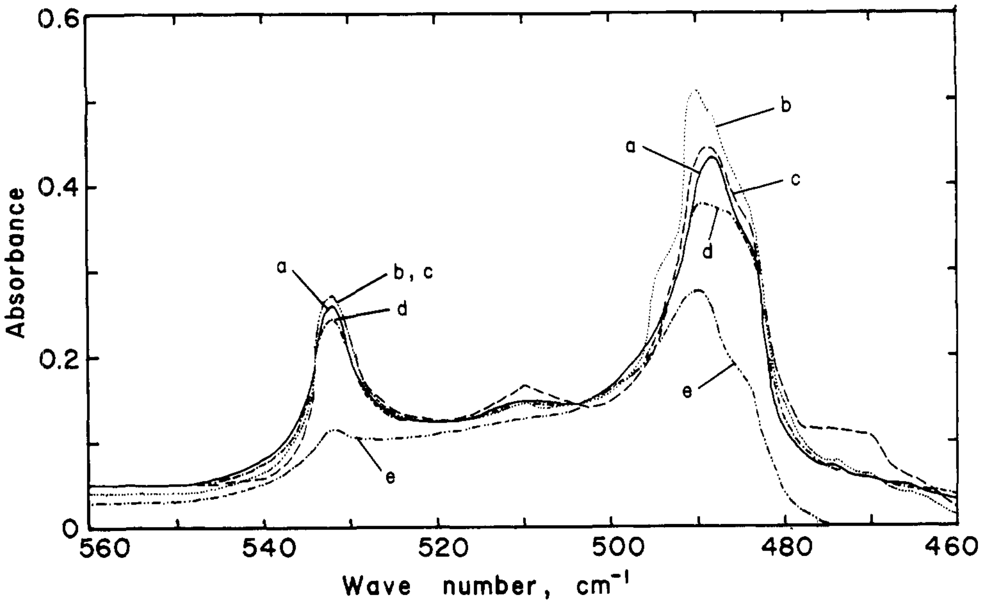

Figure 3. IR spectra of the polymer films: (a) PVF_2; (b) PVF_2/PVF (88.5–11.5%); (c) PVF_2/PVF (70–30%); (d) PVF_2/PMMA (90–10%); (e) PVF_2/PMMA (50–50%). All films were heated at 200 °C for 30 min after casting from DMF solutions.

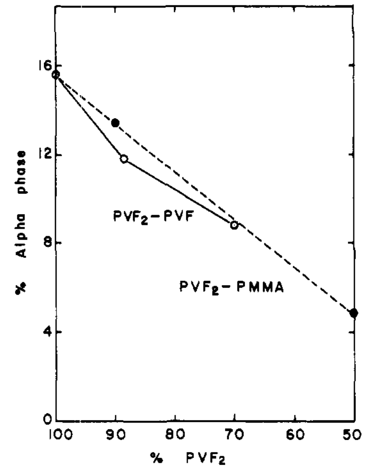

Figure 4. Proportion of α phase as a function of composition.

Chemicals No. 3021). Samples were poled under a dc electric field of 10^6 V cm^{-1} for 30 min at 80 °C. The electric field was removed and the sample was kept at the poling temperature for approximately 15 min before it was cooled to room temperature. The pyroelectric current was measured in a manner previously described.[27] X-ray diffraction patterns of the films were obtained using a Cu Kα radiation at 40 kV and 18 mA for 15 h. IR spectra were recorded using a Perkin-Elmer 225 spectrophotometer.

Results and Discussion

The changes of the pyroelectric coefficients with composition of polymer blend are shown in Figure 1. In PVF_2/PMMA the pyroelectric coefficient decreases monotonically as the PMMA content increases and vanishes when the PMMA content is greater than 50%. Films of PVF_2/PMMA blends could be easily stretched. The pyroelectric coefficients in the stretched films were about twice those in the unstretched films, and these coefficients also decreased monotonically as the content of PMMA was increased. In PVF_2/PVF, the pyroelectric coefficient shows a maximum at 11.5% PVF content. On increasing the PVF content further, a decrease was observed which approached the value of the pyroelectric coefficient in pure PVF, 0.30 nC K^{-1} cm^{-2}. The PVF_2/PVF films were relatively brittle and all attempts to stretch them were unsuccessful.

X-ray diffraction patterns of pure polymers and their blends with other polymers are shown in Figure 2. Although many papers[13-19,21,23,28] have been published concerning polymorphism in PVF_2, the actual designation of the β and γ forms varies from author to author. Gal'perin et al.[18] reported characteristic x-ray diffraction patterns for each form of PVF_2, and the x-ray diffraction pattern of our β-PVF_2 (Figure 2a) is identical with that of Gal'perin's β form. IR spectra of the samples (shown in Figure 3) were taken for cross-checking purposes. The IR spectrum of our β form is in good agreement with data in the literature.[13,17,23]

The cast films of pure PVF_2 show an x-ray diffraction pattern (Figure 2b) which is very similar to the pattern obtained with the α form.[18] However, since the film has been heated above its melting point, it must also contain a certain amount of β and γ forms.[17] PVF_2 does not seem to be compatible with PVF and the x-ray diffraction patterns of these blends give the characteristic peaks of each component (Figure 2c and 2d). On the other hand, PVF_2 is compatible with PMMA and the characteristics of each component have almost disappeared from the x-ray diffraction patterns of the 50:50 mixture (Figure 2g).

Two difficulties which arise in analyzing the data concern the separation of the area under the diffraction curves into crystalline and amorphous components and the determination of the amount of each phase. There seems to be no unique and generally accepted method for this analysis. However, several empirical methods[18,28,29] appear to work satisfactorily. A simple method which has been established by Gal'perin and his co-workers[18] has been applied in this work, in which percent crystallinity is obtained simply by measuring the percent of the area in the diffraction patterns corresponding to each crystalline phase.

In these diffraction patterns, the α form shows peaks at $2\theta = 18.2$, 18.8, 20.4, and 27.0°; the β form leads to peaks at $2\theta =$ 18.8 (very weak) and 20.5°; and the γ form leads to peaks at $2\theta = 18.8$ and 20.5°.[18] It is questionable if the small peak at $2\theta = 27°$ in Gal'perin's work is really due to the γ form or due to a small amount of the α form in the sample. We may with confidence consider the peak at $2\theta = 27°$ to be purely due to the α form. The relative area of the α peak, S_α, is plotted as a function of composition in Figure 4. Since the peaks in the range of $2\theta = 17$ to 21° are due to all three of these forms, we

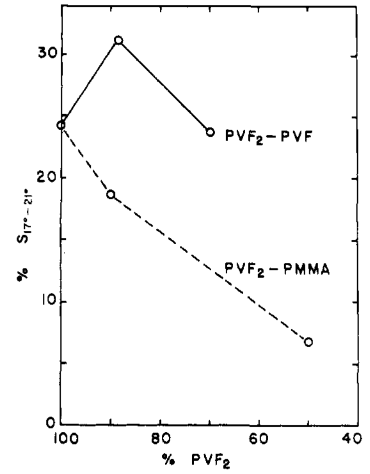

Figure 5. Change of S_{17-21° with composition.

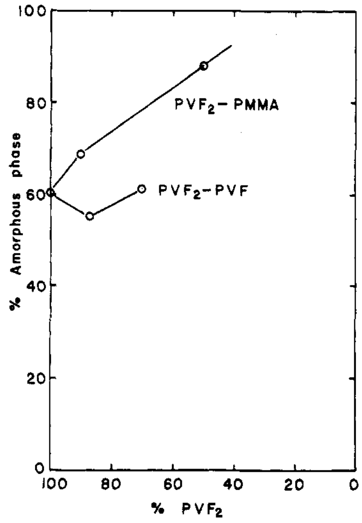

Figure 6. Proportion of amorphous phase as function of composition.

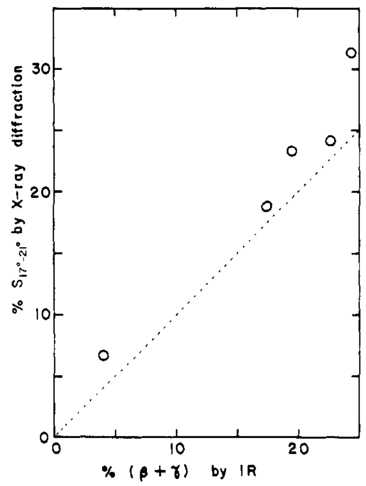

Figure 7. Comparison of S_{17-21° and percent ($\beta + \gamma$) obtained from IR spectra.

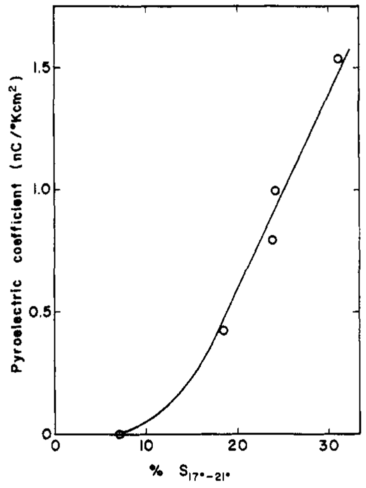

Figure 8. Correlation between pyroelectric coefficient and S_{17-21°.

can not consider them separately. The change of the relative peak area, $S_{17^\circ-21^\circ}$, with composition is shown in Figure 5.

In the PVF$_2$/PMMA blends, the amount of amorphous phase increases almost linearly with the PMMA content (Figure 6), while at the same time the amount of the crystalline phases decreases (Figures 4 and 5) and at 50% PMMA, the sample becomes almost completely amorphous (Figure 6). In PVF$_2$/PVF blends, the amount of amorphous phase stays more or less at a constant level (Figure 6). However, the amount of the α phase decreases as the PVF content increases (Figure 4). It is interesting to note that the relative peak area in the range of $2\theta = 17$ to 21°, S_{17-21°, shows a maximum at 11.5% of PVF content (Figure 5).

A similar change is observed in the IR spectra (Figure 3). The peaks at 532 and 510 cm^{-1} are due to the α and β forms, respectively.[13,17,23] All the IR spectra were normalized for the same amount of pure PVF$_2$ per unit area (1 mg of PVF$_2$ cm^{-2}). The α peak at 532 cm^{-1} is relatively well separated from other peaks. Absorption by the 50–50 mixture of PVF$_2$/PMMA (Figure 3e) is similar to the absorption by molten PVF$_2$[31,32] and is therefore assumed to be due to the amorphous phase. The peak at 510 cm^{-1} is considered to be due to absorption by β and amorphous phases. The absorption around 490 cm^{-1} is due to overlap of several different absorptions. Most of the absorption by the γ phase and some by the amorphous phase appears around 490 cm^{-1}.[13,31,32] It is interesting to note that the amount of β phase seems to increase largely at the expense of the γ phase (Figures 3b and 3c). The peak height of the IR spectra was calibrated with respect to the x-ray diffraction data. The percent crystallinity of ($\beta + \gamma$) obtained in this way shows good agreement with that from x-ray diffraction data (Figure 7).

Since the amount of the α and amorphous phases is not closely correlated with the pyroelectric coefficients, it may be inferred that these phases are not pyroelectric. On the other hand, S_{17-21° changes in a fashion similar to the change in the pyroelectric coefficient as the composition changes. Since S_{17-21° represents the amount of crystalline phase and the α phase is already known to be nonpyroelectric, the pyroelectricity is mainly due to the β and γ phases. The relationship between the pyroelectric coefficient and S_{17-21° is shown in Figure 8. A similar correlation is obtained between the pyroelectric coefficient and the percent ($\beta + \gamma$) estimated by IR spectroscopy (Figure 9).

Consequently the pyroelectricity in PVF$_2$ is mainly attributed to the β and γ phases and the contribution by the α and amorphous phases is negligible. This fact strongly supports the dipole-reorientation mechanism for pyroelectricity in PVF$_2$. It is not possible to determine the differences in activity between β and γ phases, and since these two phases have similar structures, they might be expected to have comparable pyroelectric activity.

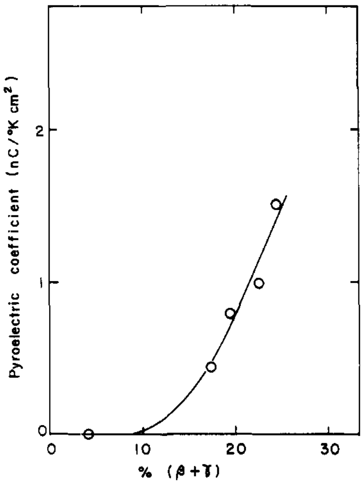

Figure 9. Correlation between pyroelectric coefficient and percent ($\beta + \gamma$) phases as determined by IR method.

Three possible mechanisms are considered for the dipole-reorientation process: (1) rotation of the individual chain around its own chain axis; (2) rotation of the polar domains;[30] and (3) a combination of (1) and (2). NMR,[33-35] dielectric,[34-38] and mechanical[39] relaxation studies have shown that restricted rotations are allowed in the crystalline phases as well as in the amorphous phases. Furthermore, the onset of rotational motion in the α phase occurs at a lower temperature (~70 °C at 110 Hz)[35] than in the β phase (~110 °C at 110 Hz).[35] In the amorphous phase, motion occurs at an even lower temperature.[33-35] If the individual chains could rotate around their own chain axes and retain this orientation, then they should exhibit some pyroelectricity. It would be reasonable to assume that the easier it is to rotate the chains, the faster the depolarization process would be. Therefore, we suggest that the amorphous and α phases are not able to retain enough polarization to give any observable pyroelectric current in the second heating cycle.

The crystalline phases are of course dispersed in the amorphous phase and the polymer chains extend into the amorphous phase. Since the amorphous phase is relatively fluid at temperatures well above the glass-transition temperature of the polymer, partial rotation of the polar domains can be expected. In uniaxially stretched PVF$_2$, the remanent polarization at room temperature is about 4×10^{-3} C cm^{-2}.[5] This is equivalent to about 3% orientation assuming pure β phase for the uniaxially stretched film. In the PVF$_2$/PMMA blends, the pyroelectricity becomes zero before $S_{17\text{-}21^\circ}$ becomes zero (Figure 8). This fact may be explained as follows. When the percent PMMA increases, the formation of α phase is favored over the formation of other crystalline phases, and the fraction of the pyroelectric phases becomes proportionately smaller. At the same time only a small amount of PVF$_2$ can crystallize so that the average size of crystalline domains becomes very small. Accordingly, the torque exerted on the polar crystallites is too small to align them along the direction of the applied electric field.

In conclusion, the correlations observed between pyroelectric activity and percent of $\beta + \gamma$ crystalline phases in polymer blends of PVF$_2$ is consistent with a dipole reorientation model. It would be highly fortuitous if the extent of trapped charge and its distribution correlated with crystallinity in blends with both PVF$_2$ and PMMA, and this letter explanation seems unlikely.

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