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Direct Evidence for Cocrystallization in Binary Mixtures of Ferroelectric Copolymers

Recently, increasing attention has been devoted to polymer mixtures from both the theoretical and the experimental points of view. Most polymer blends are incompatible because the contribution from the mixing entropy is very small as a result of the large degree of freedom of polymer chains. Miscibility between two *amorphous* polymers has been demonstrated by many researchers and studied intensely, especially in relation to phase-separation dynamics. Miscibility between *crystalline* and *amorphous* polymers has also been examined, and a number of compatible blends are known (e.g., poly(vinylidene fluoride)/poly(methyl methacrylate)² or poly(ϵ -caprolactone)/polystyrene³). These two categories of polymer blend have been reviewed extensively.^{4,5}

However, only a few studies have been reported on the miscibility between two *crystalline* polymers, and cocrystallization within a single lattice is extremely rare and in many cases questionable. Commonly, the necessary conditions for cocrystallization are thought to be (a) miscibility in the melt and (b) similarity in crystalline structures of the individual constituents. Polymers that might satisfy such conditions have been sought among those having similar chemical compositions. For example, poly(vinyl fluoride) (PVF) and poly(vinylidene fluoride) (PVF₂) had been considered for over 20 years to cocrystallize within a single lattice.^{6,7} However, recent evidence⁸ indicates that these two polymers are in fact immiscible in both the amorphous and the crystalline states. Ethylene-propylene-diene rubbers of very low crystallinity were reported⁹ to undergo only partial cocrystallization with branched (but not with linear) polyethylene. Poly(butylene terephthalate) showed a single melting endotherm with one composition of its segmented block copolymer with tetramethylene oxide, although cocrystallization could not be demonstrated by X-ray diffraction because of the similarity in the diffraction patterns of the two components of the blend.¹⁰ Very recently,¹¹ blends of poly(ether ketone) and poly(ether ether ketone) have been reported to be miscible in the crystalline phase on the basis

of their melting behavior, although the glass-transition temperatures of the two constituents are too close to allow definitive confirmation of compatibility.

Other crystalline polymers that might at first be thought of as forming compatible crystalline blends actually do not. For example, poly(vinylidene chloride) copolymers are compatible with a variety of polyesters only in the amorphous phase; the crystalline morphology shows separate populations of the two constituents.¹² The same is true for blends of isotactic polystyrene with poly(2,6-dimethylphenylene oxide).¹³ In blends of PVF₂ with stereoregular poly(methyl methacrylates) (PMMA), only the former crystallizes.¹⁴ And isotactic and syndiotactic PMMA do not form a true blend, but rather a bimolecular complex consisting of a double-stranded helix with the syndiotactic chain wrapped around the isotactic one.¹⁵

On the other hand, if a blend of two crystalline polymers is studied in which *both* crystalline phases undergo solid-state transformations (such as Curie transitions) and if the temperatures of such transitions depend strongly on the crystalline structure, there exists the possibility for a clear and unequivocal determination of cocrystallization within the same lattice.

In most materials that are miscible in the melt the system undergoes microscopic phase separation below the melting point; as a result, two types of crystal, having lattice dimensions characteristic of the individual components, coexist independently. In some cases (e.g., Cu and Ni) the two components can form *solid solutions*, in which they remain miscible even below the melting point, thus cocrystallizing within a *single* lattice. Such coexistence within the same lattice is very rare, especially in polymeric crystals because they are stabilized by van der Waals forces, which are of very short range. Therefore, small lattice mismatches result in high energetic states. In polymeric blends, isomorphic crystallization should thus be favored when the crystal structures of the two components are very similar but especially when they already contain some disorder which should render them more tolerant of slight additional mismatch.

In this sense, ferroelectric copolymers of vinylidene fluoride and trifluoroethylene (VF₂/F₃E) differing in composition represent some of the best candidates for unambiguous determination of cocrystallization, for the following reasons: (1) their crystalline structures are very similar; (2) they already contain a degree of intramolecular disorder stemming from the random sequencing of VF₂ and F₃E units; and (3) they undergo Curie transitions whose temperatures are *very sensitive* to composition.^{16,17} Because of the solid-state nature of these transitions, it is possible to probe molecular mixing *unequivocally*: In the case of phase separation upon crystallization, *two* Curie transitions should appear, whereas true cocrystallization should yield only *one* transition.

The samples investigated here were three random copolymers of vinylidene fluoride/trifluoroethylene (VF₂/F₃E), blended in equal weights by casting from solution in methyl ethyl ketone, followed by vacuum drying. Three VF₂/F₃E mixtures were examined: 52/48 mol % + 65/35 mol % (termed M1); 65/35 mol % + 73/27 mol % (M2); and 52/48 mol % + 73/27 mol % (M3). Thermal studies were performed by differential scanning calorimetry at a rate of 10 °C/min. Structural studies were made by wide-angle X-ray diffractometry by using Ni-filtered Cu K α radiation at a scanning speed of 0.25° 2 θ /min. The miscibility of these copolymers in the melt was examined by direct observation under a phase-contrast microscope. No phase separation was found in any of our mixtures at

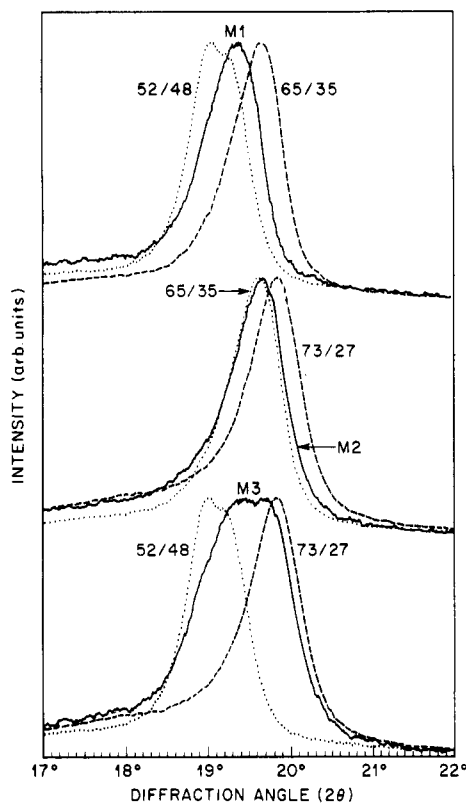


Figure 1. X-ray diffractometric scans from $\text{VF}_2/\text{F}_3\text{E}$ copolymers of the indicated compositions and their mixtures (solid line).

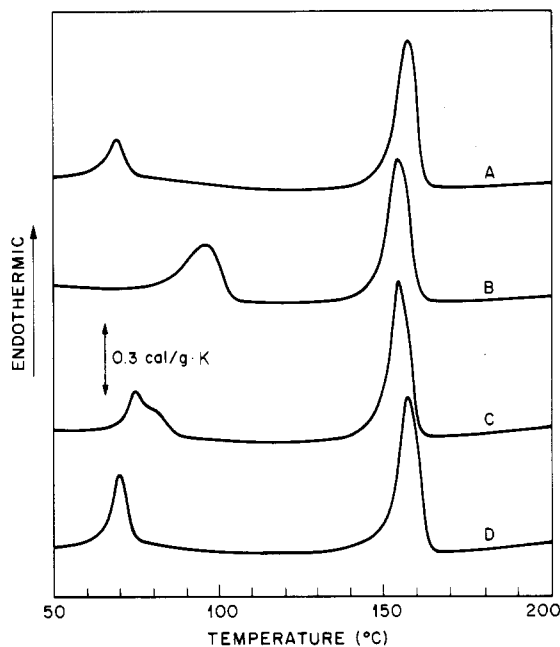


Figure 2. DSC scans from $\text{VF}_2/\text{F}_3\text{E}$ copolymers: 52/48 mol % (A), 65/35 mol % (B), and their mixture quenched rapidly (C) or crystallized at 120 °C (D).

temperatures at least up to 200 °C.

The results of our X-ray diffraction studies are shown in Figure 1 for samples in the form of thin films that had been rapidly quenched to room temperature from the melt. These diffraction peaks arise from intermolecular packing in the ambient-temperature ferroelectric phase of the copolymers. Mixtures M1 and M2 show a sharp single X-ray peak, intermediate in spacing between those of the individual copolymers and clearly different from their superposition. However, mixture M3 has two peaks that closely approach those of the individual copolymers. These X-ray results indicate that the two polymers crystallize in a

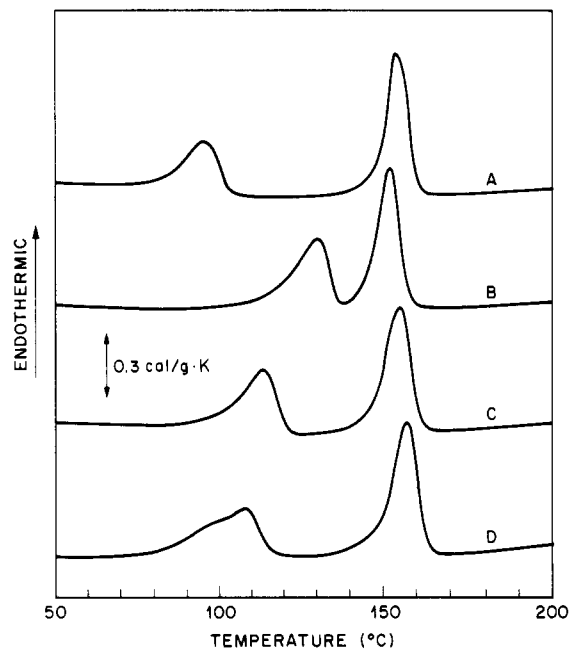


Figure 3. DSC scans from $\text{VF}_2/\text{F}_3\text{E}$ copolymers: 65/35 mol % (A), 73/27 mol % (B), and their mixture quenched rapidly (C) or crystallized at 120 °C (D).

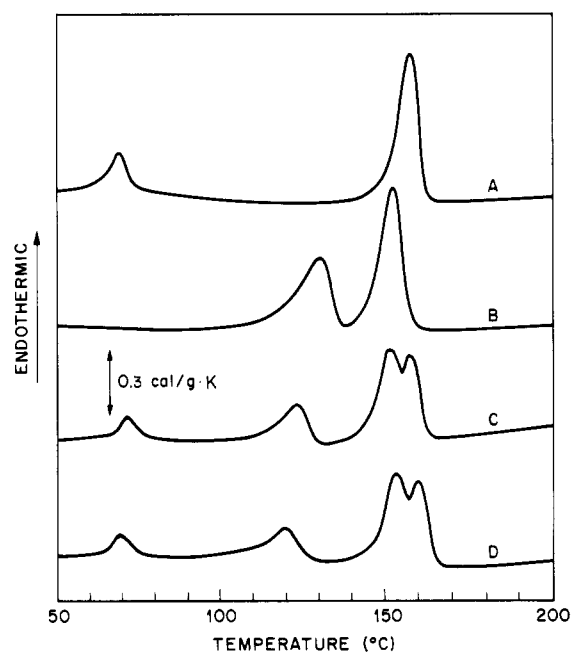


Figure 4. DSC scans from $\text{VF}_2/\text{F}_3\text{E}$ copolymers: 52/48 mol % (A), 73/27 mol % (B), and their mixture quenched rapidly (C) or crystallized at 120 °C (D).

common lattice in the case of M1 and M2, but not in the case of M3. However, even in M3 the peak from the blend is sharper than a simple summation of the two peaks from the constituents, indicating some degree of mixing in the crystals.

The results of our DSC measurements are seen in Figures 2–4. In Figures 2 and 3, mixtures M1 and M2 are seen to have only one ferroelectric transition and only one melting point. The Curie transition is shifted to a temperature intermediate between the transition temperatures of the two copolymers. We should note here that DSC results from a blend similar to our M2 have very recently been presented by Davis, DeReggi, and Chen,¹⁸ who also observed single Curie and melting peaks and interpreted them as indicating cocrystallization. Contrary to the behavior of M1 and M2, mixture M3 shows two ferroelectric

transitions and two melting points (Figure 4). These findings are fully consistent with our X-ray results, and together they demonstrate clearly the existence of molecular mixing between two polymers inside a crystal lattice.

As seen in Figures 2-4, specimens of blends crystallized at 120 °C have higher melting temperatures but lower Curie temperatures than their rapidly quenched counterparts. This is in exact agreement with the behavior found earlier by Green et al.¹⁹ for *individual* copolymers. The dependence of the Curie transition on crystallization conditions is different between M1 and M2. In mixture M1, a single symmetric DSC peak appears for the sample that was crystallized at high temperature, i.e., above the Curie point, whereas an additional shoulder is seen after a rapid quench. On the other hand, in M2 a shoulder is seen when the sample had been crystallized above the Curie point, but not in the case of rapid quenching. In the latter case, the 65/35 mol % VF₂/F₃E copolymer is known^{20,21} to exhibit a double-Curie endotherm when crystallized at temperatures above ca. 100 °C; therefore, the appearance of the shoulder in curve D of Figure 3 is probably unrelated to the state of mixing of the two copolymers. In general, these various mixing effects are expected to depend upon the crystalline structures of the constituents, as well as upon kinetic factors. With respect to the first, we should note that crystallization at high temperatures occurs in the *paraelectric* phase, so that the ferroelectric lattice seen in the diffractograms of Figure 1 is adopted by the molecules only as a result of a solid-state transformation during cooling. Therefore, the difference in crystalline structures between the ferroelectric and paraelectric phases of both copolymers, as well as the associated differences in dipole-dipole interactions, will also play a role in the type and extent of mixing. These effects are being investigated.

In Figures 2-4 we also observe that the Curie temperature of mixture M1 is very close to that of the 52/48 mol % copolymer, and significantly sharper, whereas that of M2 is in the middle of the range between those of the individual constituents. The lattice spacing of M1 obtained by X-ray diffraction is located somewhat nearer to that of the 52/48 mol % copolymer, while that of M2 is very close to the spacing of the 65/35 mol % sample. These results are consistent with the expectation that the structure of the mixed crystals would be dictated primarily by the more disordered component.

The existence of two types of crystal in the M3 mixture (Figure 4) indicates a threshold in chemical and lattice differences with regard to cocrystallization. The slight decrease of the upper Curie temperature suggests that a small amount of the 52/48 mol % copolymer is contained in the crystals of the 73/27, thus introducing additional disorder. In this context, we found no compatibility in 50/50 wt % blends of these copolymers with *homopolymer* PVF₂ even in the melt.

In conclusion, our results from X-ray diffraction and DSC demonstrate cocrystallization within the same lattice by two polymers that possess similar chemical and crystalline structures. This similarity has to be close, as indicated by the formation of separate phases in blends of the 52/48 and 73/27 copolymers. Nevertheless, demonstration of such cocrystallization even among very similar macromolecules is remarkable, inasmuch as it has not been obtained in blends of other very similar polymers. For example, blends of ethylene/vinyl chloride copolymers studied over the full range of composition have been found²² to be incompatible when one or both of the con-

stituents is crystalline, even for compositions that differ by only a few percent. Even *deuteriated* polymers are generally incompatible with their protonated counterparts and form separate crystals (as, e.g., in polyethylene²³).

We have also clearly demonstrated that solid-state transformations such as Curie transitions are very sensitive to the mixing state in crystals and therefore constitute potentially an ideal probe of cocrystallization in the same lattice. Modification of phase transitions, such as ferroelectric, ferromagnetic, or superconducting, induced by cocrystallization of two materials may be general in the condensed state.

A more detailed study of the compositional and temperature dependence of compatibility in our ferroelectric polymers, of their phase diagram, and of the dielectric and ferroelectric properties of their blends will be published elsewhere.

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Registry No. (VF₂)(F₃E) (copolymer), 28960-88-5.

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Low Polydispersity Homopolymers and Block Copolymers by Ring Opening of 5,6-Dicarbomethoxynorbornene

In general, classical metathesis catalysts will not tolerate functionalities such as the carbonyl group.¹ In some cases