polystyrene gel columns, Shodex A802, A804, A806, and A807 (Showa Denko, Co., Japan) was used, whose exclusion limit molecular weight had been estimated to be ca. 2×10^8. The calibration curve for $\bar{M}_w$ and $\bar{M}_n$ calculations was obtained with 10 monodispersed polystyrenes whose $\bar{M}_n$'s were in a range 3.7×10^4–6.8×10^6. Intrinsic viscosities were measured in toluene solution at 30 °C.

Registry No. $(CH_3)_3SiC{\equiv}CCH_3$ (homopolymer), 87842-32-8; $TaCl_5$, 7721-01-9; Ph_3Bi, 603-33-8; Ph_3Sb, 603-36-1; Ph_4Sn, 595-90-4; Bu_4Sn, 1461-25-2; Ph_3SiH, 789-25-3; Et_3SiH, 617-86-7; $NbCl_5$, 10026-12-7.

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(8) The time course of intrinsic viscosity in the polymerization by $TaCl_5$ was reported.[2b] Here the time–$\bar{M}_w$ relationship is shown for comparison.

Ferroelectric Properties of a Copolymer of Vinylidene Fluoride and Trifluoroethylene Blended with Poly(methyl methacrylate)

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Received April 16, 1986

Random copolymers of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) are known to exhibit many features characteristic of ferroelectrics.[1-6] Although domain structures have not been observed so far, the system shows distinct transitions in its properties near the Curie temperature, T_c. For example, as the temperature approaches T_c from below, both the remanent polarization and the piezo- and pyroelectric activities drop sharply to zero,[1-4] the electric susceptibility exhibits a temperature dependence in accordance with the Curie–Weiss law,[1,6] and the molecular conformation changes from the trans-zigzag form to the gauche form;[7,8] furthermore, there is an increase in the crystal lattice spacing[1] as well as a change in the specific heat.[5] In addition to these transition phenomena, the copolymer system displays a wide variation in the melting point over the entire range of composition.[9] Since the conformational change at T_c primarily arises from intramolecular interactions whereas the melting behavior involves both intra- and intermolecular interactions, it is of interest to examine how the ferroelectric and other properties of the copolymers may be affected by mixing them with a compatible polymer. In this paper, we report the results of a brief study made on the blends of P(VDF/TrFE) and poly(methyl methacrylate) (PMMA),

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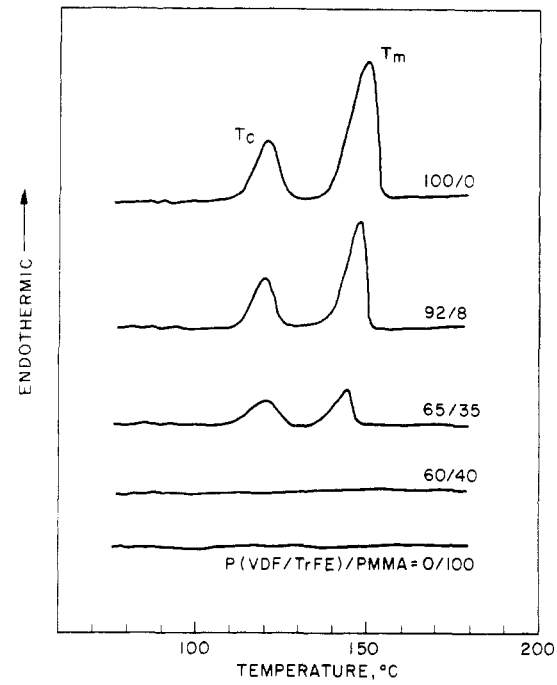

Figure 1. DSC thermograms of P(VDF/TrFE), PMMA, and their mixtures obtained at the scanning rate of 20 °C/min.

which have been found to be mutually compatible in the melt state. While our study was inspired by a previous investigation on blends of poly(vinylidene fluoride) (PVDF) and PMMA,[10] the homopolymer PVDF does not display ferroelectric transitions below its melting point; therefore, it does not allow us to carry out the type of study described in this paper.

Experimental Section

A copolymer of vinylidene fluoride and trifluoroethylene (P(VDF/TrFE)) having a molar compositional ratio of 78.5/21.5 was kindly supplied by Central Glass Co., Japan. It had an $\bar{M}_n$ value of 6.73×10^4 and a polydispersity of 2.18. Atactic PMMA with an $\bar{M}_n$ of 1.27×10^4 and a polydispersity of 2.18 was supplied by Mitsubishi Rayon Co. Ltd., Japan.

Films of P(VDF/TrFE), PMMA and their mixtures were cast from *N,N*-dimethylacetamide solution (3 g/100 mL) onto glass substrates maintained at 60 °C and subsequently allowed to dry slowly at room temperature. The average thickness of the films was about 80 μM. Unless otherwise noted, the compositional ratio of P(VDF/TrFE) to PMMA will be reported on the weight basis.

Calorimetric study was carried out with a Rigaku-Denki Model PTA-10 differential scanning calorimeter. Prior to temperature scanning, each sample (ca. 5 mg) was heated at 200 °C for 30 min to ensure complete melting of crystals and then cooled to room temperature at a rate of 10 °C/min.

Measurements of the piezoelectric constant were made at a frequency of 10 Hz with an apparatus described in ref 11. Films for these measurements were first metalized with aluminium electrodes (ca. 100 nm thick) on opposite faces in the central region covering an area of 5×8 mm^2 and subsequently poled at 100 °C under a dc field of 20 MV/m for 30 min.

Results and Discussion

Thermograms of P(VDF/TrFE), PMMA, and several of their blends obtained at a heating rate of 20 °C/min are shown in Figure 1. As expected,[4,9] the copolymer itself exhibits two prominent endothermic peaks; the one at 150.5 °C corresponds to the melting event while the other at 120 °C corresponds to the Curie transition.[4,9] When PMMA is added to the copolymer, both peaks diminish progressively and disappear completely as the PMMA content, ϕ_w, exceeds 40 wt %; however, while the melting point shifts continually toward lower temperatures, the

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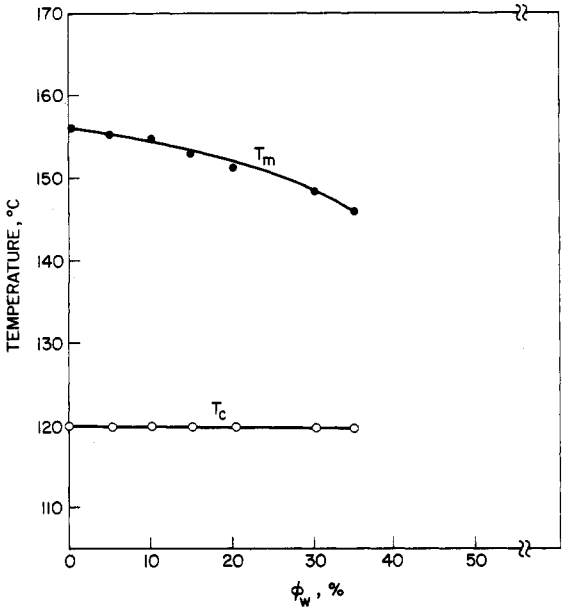

Figure 2. Plots of the melting point (T_m) and the Curie temperature (T_c) of P(VDF/TrFE)/PMMA mixtures as functions of weight fraction (ϕ_w) of PMMA.

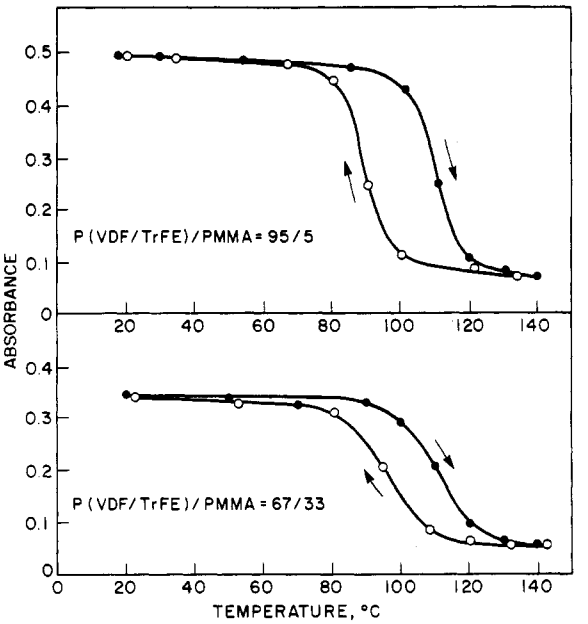

Figure 3. Infrared relative absorbances at 848 cm^{-1} for P(VDF/TrFE)/PMMA mixtures having compositions of 95/5 (upper panel) and 67/33 (lower panel).

Curie point T_c remains practically unchanged. This can be seen readily in Figure 2, where the melting point (defined as the temperature at which the last detectable trace of crystallinity disappears) and the Curie temperature (defined as the peak temperature of the transition) are plotted as functions of ϕ_w.

The depression of T_m in the mixture is a clear indication of compatibility between PMMA and the copolymer above its melting point. Nishi and Wang[10] have observed the depression behavior in the binary PVDF/PMMA system and attributed this to the thermodynamic effect of mixing between two compatible components in the melt state. Values of the interaction energy density B and the interaction parameter χ_{12} were determined according to the procedure established in ref 10 and found to be $B = -2.57$ cal/(cm^3 of PMMA) and $\chi_{12} = -0.261$ at 150 °C. Comparison of these numerical results with the corresponding values for the PVDF/PMMA system ($B = -2.98$ cal/(cm^3 of PMMA) and $\chi_{12} = -0.295$ at 160 °C) shows that the latter system has larger negative values and, therefore, is more compatible than our system. This is perhaps not too surprising since TrFE, one of the components in the copolymer, is not compatible with PMMA.

The invariance of the Curie temperature is an interesting feature which can be explained by the fact that T_c is associated with conformational change of the chain segments from the extended all-trans to the contracted gauche form within the crystals.[7,8] This transformation occurs in the solid state; therefore, it should not be affected by the presence of PMMA, which coexists with the amorphous P(VDF/TrFE) fraction outside the crystal region. To confirm that the Curie transition is indeed associated with the conformational change, thin films of the blends were prepared and their infrared absorption for the trans bonds at 848 cm^{-1} was monitored as a function of temperature. Typical results for two samples with $\phi_w = 5$ and 33 wt % are shown in Figure 3. When the 5% sample (upper panel) is heated, its absorption intensity begins to decrease around 100 °C and levels off at 120 °C. However, if the sample is cooled after it reaches 140 °C, the intensity remains unchanged until about 95 °C at which it begins to recover, giving rise to a hysteresis loop. A similar hysteresis-like phenomenon is observed in the 33% sample;

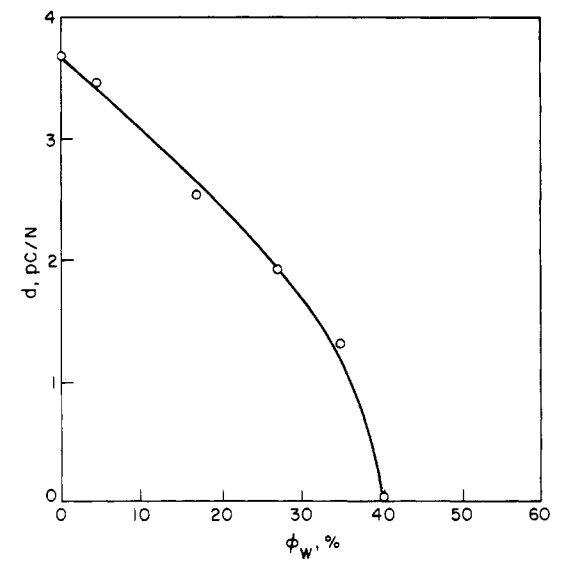

Figure 4. Plots of piezoelectric strain coefficient d ($=d_{31} = d_{32}$) of P(VDF/TrFE)/PMMA mixtures as a function of PMMA weight fraction ϕ_w.

but in comparison with the 5% sample, the intensity change is smaller, apparently because of the lower crystalline content in the sample. There was no change of absorption intensity in samples with $\phi_w > 0.4$, apparently because they did not contain any crystals (cf. Figure 1). This hysteretic behavior has been observed in previous studies using X-rays[8] and has been related to the first-order phase transition at the Curie temperature.

The influence of PMMA on the piezoelectric property of the mixture is shown in Figure 4, where the d ($=d_{31} = d_{32}$) coefficient is plotted as a function of ϕ_w. As would be expected from the crystalline origin of piezoelectricity, the d value drops sharply with the addition of PMMA to the copolymer and disappears almost completely as ϕ_w, exceeds 0.4, the range of PMMA fraction in which both the crystallinity and the Curie temperature disappear in the mixtures. However, when the d values are plotted as a function of heat of fusion H_m, the plot shows a nonlinear behavior (Figure 5), indicating that the piezoelectric ac-

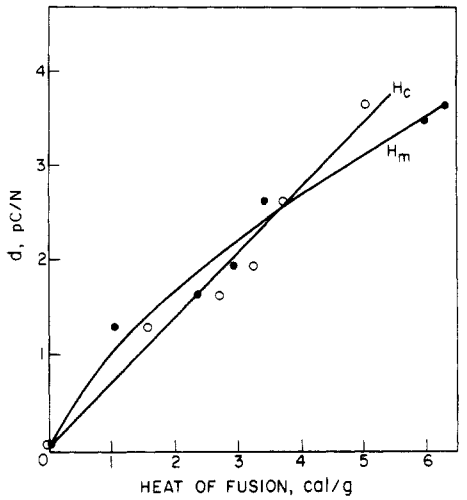

Figure 5. Plots of piezoelectric strain coefficient d as a function of heat of fusion either at the melting, H_m (●), or at the Curie transition, H_c (○).

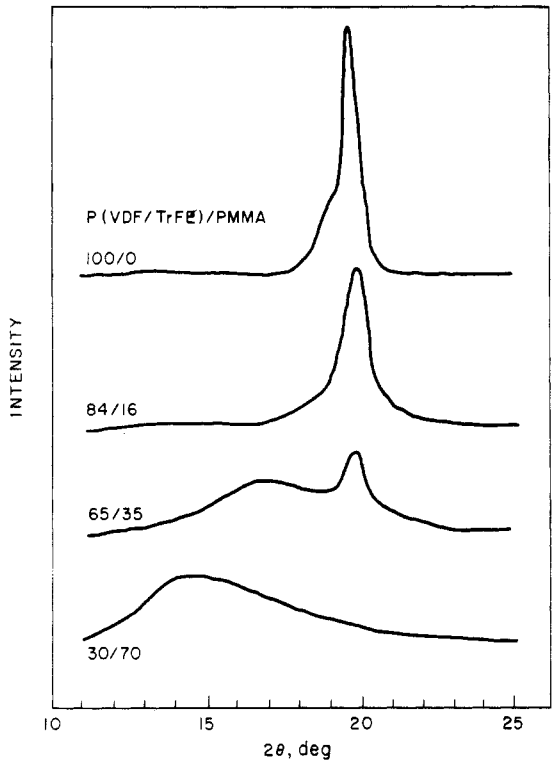

Figure 6. X-ray scans of P(VDF/TrFE)/PMMA mixtures with various compositions.

tivity is not proportional to the total crystalline content of the mixture. On the other hand, a linear relationship is observed (Figure 5) when we plot the d value as a function of H_c, the area under the curie transition peak in Figure 1. This result strongly suggests that the crystalline region contains both ferroelectric and paraelectric phases, but only the ferroelectric fraction contributes to polarization.

The above conclusion is also supported by the X-ray data (Figure 6), which show a peak corresponding to the ferroelectric phase at 19.7 2θ and a shoulder corresponding to the paraelectric phase at 18.8 2θ for the copolymer sample. As PMMA is added to the copolymer, both the ferroelectric and paraelectric peak diminished, but the suppressing effect is much stronger in the paraelectric than in the ferroelectric phase. (The peak near 16.5 2θ for the 65/35 mixture corresponds to the amorphous halo, which is seen to shift to a lower angle as ϕ_w is increased, e.g., the bottom curve of the figure.) This selective suppression is also evident in Figure 5, where the d–H_m plot crosses over the d–H_c plot as the heat of fusion decreases, i.e., as the PMMA fraction in the mixture increases.

In summary, our study showed that PMMA is compatible with P(VDF/TrFE) above the melting point of the copolymer; however, while PMMA depressed both the T_m and the rate of crystallization of the copolymer, it did not affect the Curie point. We also found that the piezoelectric activity of the copolymer did not depend on the total degree of crystallinity but only on the ferroelectric fraction of crystals.

Registry No. (VDF)·(TrFE) (copolymer), 28960-88-5; PMMA, 9011-14-7.

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Homo- and Heteronuclear Two-Dimensional Correlated Nuclear Magnetic Resonance Spectra of Cellulose

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Received December 17, 1985

A substantial recent effort has been devoted to the investigation of cellulose solutions by NMR spectroscopy.[1-4] Difficulties arise in the application of the technique because of (i) the problem of dissolving cellulose, (ii) the high viscosity of the polymer solutions and hence the lack of spectral resolution, and (iii) the inadequacy of the classical assignment techniques.

To overcome these difficulties, spectral assignment can be made easier by means of two-dimensional NMR. The dissolution of cellulose is a difficult operation, owing to the existence of strong intra- and intermolecular hydrogen bonds of this highly hydroxylated polymer in its solid state. Among the new solvent systems for cellulose, *N*,*N*-dimethylacetamide (DMA) containing 5–8% lithium chloride is an aprotic solvent, which, in turn, allows observation by proton NMR spectroscopy of individual labile hydroxyl resonance signals.[5] These signals can then be used as a source of new information concerning the nature and the conformation of the polymer in solution.

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