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(24) The use of the word "phase" in this paper will take three different meanings, depending on the context: (1) the phase of a wave of electrons; (2) phase contrast in the electron microscope; and (3) domains in polymers representing separate thermodynamic phases of material. Therefore, in order not to confuse the reader, effort has been made throughout the paper to provide a clear context.

# Spectroscopic Study of Polystyrene and Poly(vinyl methyl ether) Blends

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ABSTRACT: Various incompatible or compatible polystyrene and poly(vinyl methyl ether) blends have been prepared by varying composition, solvent, and thermal history. Fourier transform infrared spectroscopic analysis of these samples has revealed definite spectral features sensitive to compatibility. The vibrations most sensitive to change in molecular environment are the CH out-of-plane vibration in PS and the $COCH_3$ vibrations of PVME.

## Introduction

Recently, there has been a large number of theoretical and practical studies attempting to better understand the phase separation behavior of polymer blends and the associated properties.[1] In our laboratory we have used primarily vibrational spectroscopy to characterize microstructures of polymer blends and their changes when samples are deformed macroscopically. These experiments, in conjunction with other physical measurements, are useful in the development of phenomenological models for deformation describing more fully the structure-property relationships of polymer blends. We have given particular attention to polystyrene (PS)/poly(vinyl methyl ether) (PVME) blends. The unusual compatibility behavior of this binary mixture is particularly interesting. A number of workers have shown that solvent, molecular weight, composition, and temperature can all affect the compatibility of these two polymers.[2-9]

Of all the possible binary mixtures, few are compatible. In these systems, favorable intermolecular interaction is a necessary requirement. However, in most cases the molecular origin of the driving force for compatibility is generally not clearly understood. Therefore, the search and characterization of molecular parameters lowering the total free energy represent important areas of study. Vibrational spectroscopy is an attractive technique for such studies. When properly assigned, the position, intensity, and shape of vibrational bands are useful in clarifying conformational and environmental changes of polymers at the molecular level. Because intrachain energy is so much higher than interchain nonbonded interactions, spectroscopic features of a single molecule as a result of molecular interaction are generally quite small. Strong interactions such as intermolecular hydrogen bonding are well documented in the literature. In most polymer blends, however, small differences in the vibrational spectra are difficult to observe directly and can only be shown in the difference spectra. The advent of Fourier transform infrared spectroscopy has made analysis of chemical mixtures by computer-calculated difference spectra quite convenient and accurate. As a result, several studies have shown specific spectroscopic features sensitive to changes in compatibility can be observed and have been used to interpret conformation or environment of polymers when blended.[10-17]

We have prepared compatible or incompatible PS/PVME films of various compositions from various solvents. In addition, phase-separated binary mixtures can be prepared at temperatures above the lower critical solution temperature (LCST). We have obtained infrared data from all these samples and have identified spectroscopic features characteristic of localized structure and environment of individual components in compatible or incompatible binary mixtures. Our results are reported here.

## Experimental Section

Atactic PS and PVME used in this study were obtained from commercial sources. PS of weight-average molecular weight, $M_w$, 233 000 with polydispersity equal to 1.06 was obtained from Pressure Chemical Co. Other narrow molecular weight distribution atactic polystyrenes of $M_w = 175\,000$, 50 000, and 37 000 were obtained from Polysciences. PVME was also obtained from Polysciences. Its molecular weights ($M_w = 99\,000$, $M_n = 46\,000$) were determined by GPC in our laboratory. In this case, polystyrene was used as standard. We found PVME as purchased contained a strong band at 1735 $cm^{-1}$. This vibration has been assigned to the C=O group stretching vibration of butethal, which can be removed by vacuum desiccation. Solvents of spectral grade were obtained commercially and used without further purification.

Thin films of the PS/PVME binary mixtures (15, 50, 64, and 84% weight fraction of PS) were prepared from solutions (approximately 3-5% by weight) by casting onto potassium bromide (KBr) windows. Compatible films were obtained from toluene solutions. Incompatible ones were cast from chloroform or trichloroethylene. The solvents were completely removed by drying in vacuum ovens at 70 °C for at least 72 h. It has been suggested that morphology of the samples may be affected by differences in concentration, extreme thinness of film prepared, and solvent evaporation rate.[5] Furthermore, band shape and relative intensities can depend on index of refraction due to dispersion effects.[13] We tried to remedy these experimental errors by preparing films under identical conditions. Thermally induced phase-separated samples were prepared by keeping the thin film on KBr in the oven at appropriate temperatures.

Infrared spectra were obtained with a Nicolet 7199 Fourier transform infrared instrument. Three hundred scans of 2-$cm^{-1}$ resolution were signal averaged and stored on a magnetic disk

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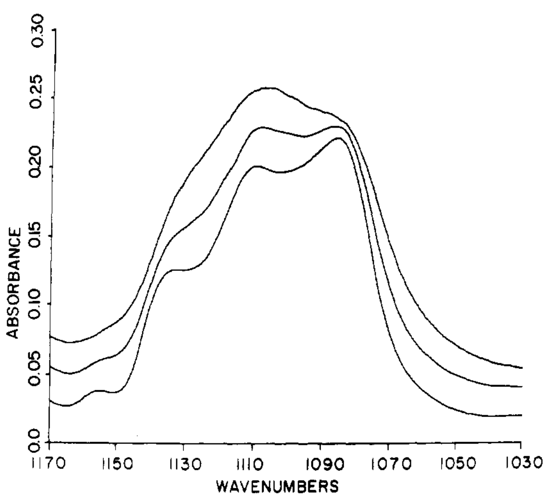

**Figure 1.** Relative intensity changes for the PVME 1100-cm$^{-1}$ bands as a function of temperature: (top) 130 °C; (middle) 25 °C; (bottom) −180 °C. The ordinate scale is applicable for the −180 °C system.

system. Entire or partial spectra can then be accessed for further analysis.

We built a sample cell that can be used to obtain infrared and Raman spectra between −180 and 200 °C. In some cases, detailed spectral features were difficult to observe at room temperature and can only be seen clearly at low temperatures. With this cell we also obtained spectra at high temperatures to follow the dynamics of thermally induced phase separation.

## Results and Discussion

To date, qualitative and quantitative data from vibrational spectroscopy have been largely used in analyzing composition or for the elucidation of localized structures. Due to the significant amount of conformational and packing disorder in polymers, even for ones of highest crystallinity, detailed spectroscopic information related to the effects of intermolecular interactions in solid polymers is difficult to obtain. Therefore, with few exceptions, the vibrational spectra obtained thus far mostly reflect regular or irregular structures of a repeat unit or an isolated chain. In a few systems, strong intermolecular interactions such as hydrogen bonding can significantly affect the band positions or intensity. In most cases, however, spectroscopic perturbations arising from interchain forces are simply too small to be observed with a high degree of confidence. The initial goal in these blend studies is to search for and characterize features sensitive to composition or degree of phase separation. It should be recognized that unless one uses the group frequency method, it is rather difficult to assign vibrational transitions of atactic polymers.

Before blends can be studied, spectroscopic features of neat polymers need to be examined at low temperatures to identify vibrations sensitive to temperature variations. When the temperature of observation is lowered, both the specificity and magnitude of intermolecular interactions increase sufficiently to enhance spectroscopic features sensitive to interchain interactions. From previous studies,[10,18] vibrations involving the oxygen atom usually exhibit high sensitivity to blend compatibility. In the infrared spectrum of PVME a strong doublet at 1085 and 1107 cm$^{-1}$ with a shoulder at 1132 cm$^{-1}$ of PVME showed the greatest change in its relative intensity when the sample was cooled or heated, as shown in Figure 1. Although the positions of the two bands did not change, their relative intensities changed substantially. The 1107-cm$^{-1}$ component dominates at high temperature whereas the 1085-cm$^{-1}$ component dominates at low temperature. In a separate experiment to show the sensitivity of this doublet to structural changes, we quenched PVME from the melt. The infrared spectrum shown in Figure 2 (observed at room temperature) did not show clear evidence of the doublet. Instead, a broad peak was observed in the 1100-cm$^{-1}$ region. The position or shape of other bands did not show such obvious sensitivity to temperature or sample history. Although the exact assignment of these two bands is not yet understood, one can obtain some information from normal vibrational analysis of model compounds. Synder and Zerbi carried out a normal vibrational analysis for a series of aliphatic ethers.[19] They showed that model compounds such as methyl ethyl ether, diethyl ether, and 1,2-dimethoxyethane all exhibit intense bands in this region. In those cases, only one component involves essentially pure C–O stretching. The other contain a significant amount of C–O stretching with contributions from methyl rocking and C–C stretching in the potential energy distribution.

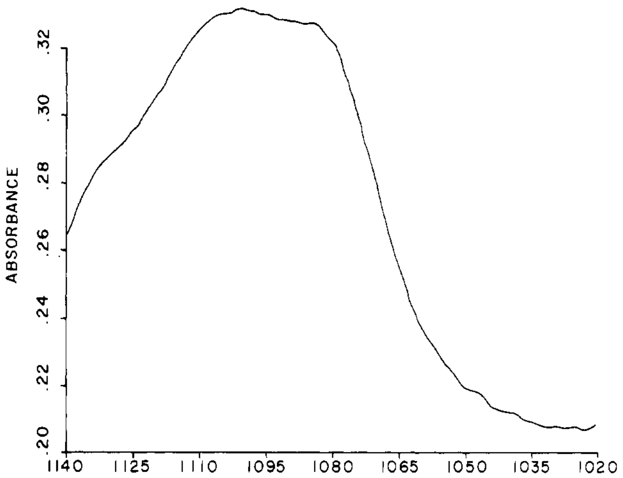

**Figure 2.** Infrared data in the 1100-cm$^{-1}$ region for the PVME film quenched from the melt.

From space-filling models it was evident that considerable rotational freedom exists for the $OCH_3$ group about the main chain. However, the exact relationship between structural differences and changes in the infrared spectrum remains unclear. Therefore, at present we can only conclude the relative intensity of this doublet with the 1100-cm$^{-1}$ region of the infrared spectrum of PVME is sensitive to structural changes and environment and, as we shall demonstrate, sensitive to compatibility or incompatibility of PS/PVME blends.

Previously, it had been established clearly that high molecular weight PS/PVME binary mixtures containing ~20–80% PS ($M_w$ > 17 500) dissolved in chloroform or TCE can be used to cast incompatible films.[2-4] For the same binary mixtures dissolved in toluene, compatible blends can be prepared. These two samples are quite different when examined visually. In one case, totally transparent films can be obtained from toluene solution. For films obtained from TCE or chloroform, phase-separated films can be seen to be grainy in appearance. The most pronounced spectroscopic difference found for PVME bands is found in the 1100-cm$^{-1}$ region. Although the frequencies of the doublet do not change, the relative intensities of the two bands in the 1110-cm$^{-1}$ region differ in the two types of samples. In these two cases we have removed the PS contribution at 1070 cm$^{-1}$ (in-plane bending) from the mixture by difference spectroscopy. The 1028-cm$^{-1}$ band of PS was used as an internal standard. As can be seen in Figure 3 for compatible blends

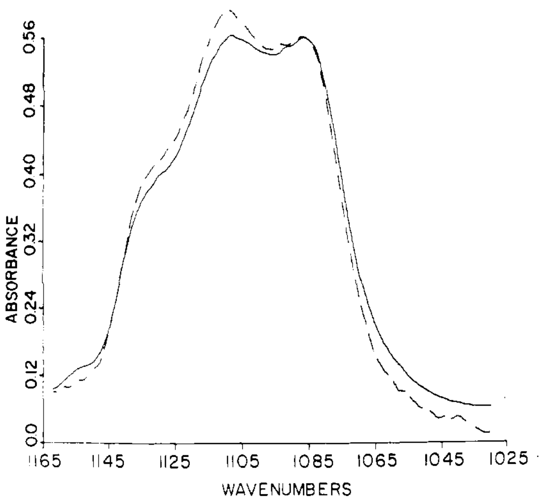

**Figure 3.** Infrared spectrum of compatible and incompatible 50/50 PS/PVME blends in the 1100-cm$^{-1}$ region: (—) compatible; (- - -) incompatible.

such as the binary mixtures obtained from toluene, the intensity of the 1085-cm$^{-1}$ band is greater than that of the 1107-cm$^{-1}$ component. For incompatible blends obtained from chloroform or TCE, the reverse is true.

Recently, Allara and co-workers pointed out that when the index of refraction of the individual components differs significantly, apparent spectral differences can arise from changing bandshape due to dispersion effects and may not be associated with the magnitude or specificity of intermolecular interactions.[13] Similar studies to clarify such systematic experimental errors of infrared transmission experiments have been carried out by Jones and coworkers.[20,21] Since we could not determine optical coefficients of the individual components and their blends easily, in our experiments, the same binary PS/PVME mixtures were used to prepare various samples. Only then can we be sure that the spectroscopic differences were dependent only on compatibility and not on composition.

In the infrared spectrum of PS, a number of bands showed small changes in position or shape when PS is blended with PVME. The band most sensitive to phase compatibility is located near 700 cm$^{-1}$. This band is generally assigned to the CH out-of-plane bending vibration.[22] It is found at 699.5 cm$^{-1}$ for film cast from toluene solutions containing equal molar amounts of PS and PVME. This is to be compared to the peak maximum located at 697.7 cm$^{-1}$ in neat PS. For incompatible blends of PS/PVME such as the film cast from TCE solutions, the peak maximum is usually found at an intermediate position between the two extremes. These differences are shown in Figure 4. Similar changes in frequency for this vibration have also been observed for PS blended with poly(2,6-dimethylphenylene oxide).[10]

We carried out additional experiments to substantiate that the spectroscopic differences found for PVME or PS are indeed associated with compatibility. Unlike the samples containing 50% PS, the binary mixtures containing 15% PS are compatible with PVME for all molecular weights and solvents. As can be seen in Figure 5, for binary mixtures containing 15% PS, the bands in the 1100- or 700-cm$^{-1}$ regions for films cast from toluene and TCE solutions are identical.

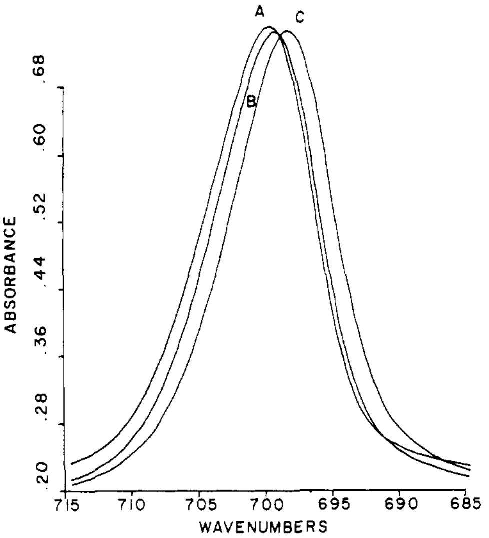

**Figure 4.** Infrared spectrum of compatible and incompatible 50:50 PS/PVME blends of PS in the 700-cm$^{-1}$ region: (A) compatible; (B) incompatible; (C) PS.

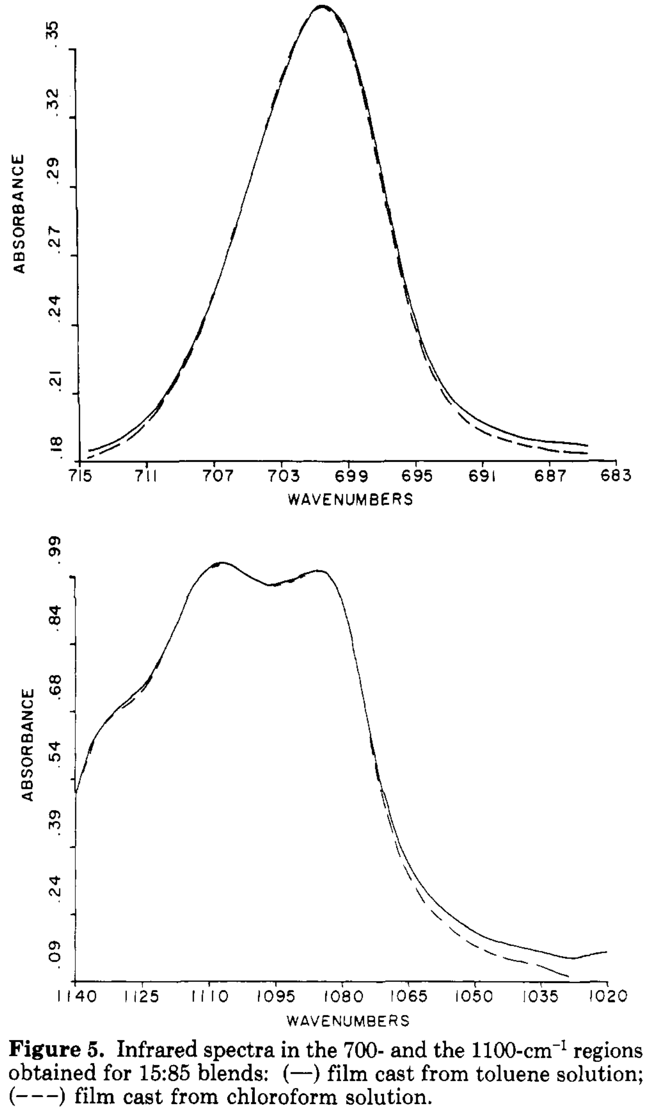

**Figure 5.** Infrared spectra in the 700- and the 1100-cm$^{-1}$ regions obtained for 15:85 blends: (—) film cast from toluene solution; (- - -) film cast from chloroform solution.

PS/PVME blends possess a lower critical solution temperature. Above this critical temperature, a compatible blend can phase separate. For the sample containing equal molar parts of PS and PVME, the initially transparent film (compatible) will turn slightly bluish at ~130 °C and then optically opalescent at approximately 150 °C (incompatible). If quenched at this stage, the two phases, one rich in PS and the other rich in PVME, would remain separated. However, if the binary mixtures were allowed to cool slowly, the two phases would return to the compatible state. Infrared spectra were obtained for binary mixtures containing equal parts of PS or PVME with different thermal histories. The spectroscopic differences observed for either PVME or PS in compatible or incompatible samples are entirely consistent with the results presented previously. This experiment further substantiates those vibrational bands which can be used to characterize the compatibility of the two components.

The molecular or structural basis for miscibility is a subject of intense scientific interest driven by the need to be able to predict a priori which polymer pairs will form miscible mixtures. Several molecular mechanisms including complex formation, charge transfer, and hydrogen-bond formation, which are know to exist in low molecular weight mixtures, also have been found in high molecular polymeric mixtures. Vibrational spectroscopy has been used to deduce the existence of dipole–dipole interactions or hydrogen bonding in PS/poly(2,6-dimethylphenylene oxide) and poly($\epsilon$-caprolactone)/poly(vinyl chloride).[10,12] The molecular level of intermixing that occurs in PS/PVME blends may include dispersion forces from several chemical groups. A negative excess volume of PS and PVME in miscible mixtures suggests the two polymers can be packed rather efficiently. As shown previously, the vibrations of PS or PVME most sensitive to changes in compatibility are associated with the phenyl ring of PS and the $COCH_3$ group of PVME. The sensitivity of the CH out-of-plane vibration in PS suggests the possible involvement of the phenyl ring in the interaction. This band was perturbed in both intensity and frequency when PS was blended with poly(2,6-dimethylphenylene oxide).[10] These spectral changes have been accounted for by a strong dipole–dipole interaction between the phenyl rings of the PS and 2MPPO.[10] From molecular models the $COCH_3$ group in PVME is fairly accessible and may indeed participate in the intermolecular interaction.

Thermal behavior of polymer blends is of great interest from both practical and fundamental viewpoints. While LCST behavior is a thermodynamic and therefore reversible phenomenon, the rates at which phase splitting and recombination occur can determine the resultant phase morphology. From nuclear magnetic resonance experiments, the morphology of the phase-separated samples can be described as microheterogeneous, where PVME and PS chains, although relatively well mixed, are not completely mixed on a segmental scale.[2] Although there are regions where PVME and PS chains interpenetrate one another, the interpenetration is inevitably limited by excluded volume and geometeric effects.

Specific absorptions in PS (700 $cm^{-1}$) or PVME (1100 $cm^{-1}$) have been demonstrated to be sensitive to compatibility. We were particularly interested in whether this evidence can be used to distinguish thermal behavior of compatible or incompatible PS/PVME blends and the structures found above LCST.

Infrared spectra were obtained for compatible or incompatible PS/PVME blends studied at various temperatures. Interpretation of the results is complicated by the fact that infrared spectra of both pure PS and PVME change when the temperature of the sample is changed. For example, the 700-$cm^{-1}$ band in pure PS shifts slightly to lower frequency when the temperature is raised from room temperature to 155 °C. Between room temperature and 120 °C the change in frequency is rather small, with the largest change occurring between 120 and 150 °C above the $T_g$ of PS. The relative intensity of the doublet in the 1100-$cm^{-1}$ region of PVME also changes significantly (Figure 1). PVME is a very flexible polymer; its infrared spectrum can change fairly abruptly at temperatures considerably lower than the ones found for PS.

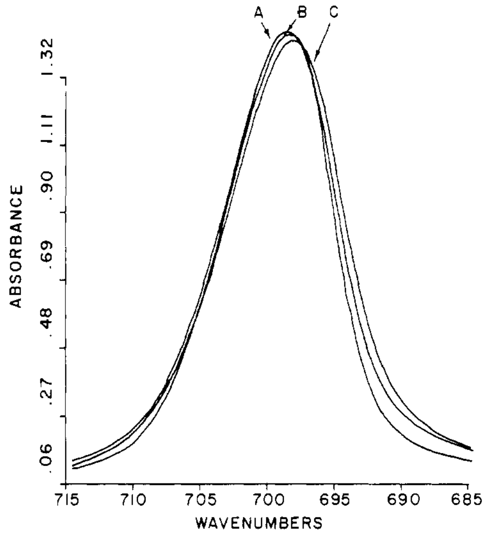

**Figure 6.** Temperature of the 700-$cm^{-1}$ PS band: (A) 25 °C; (B) 70 °C; (C) 150 °C.

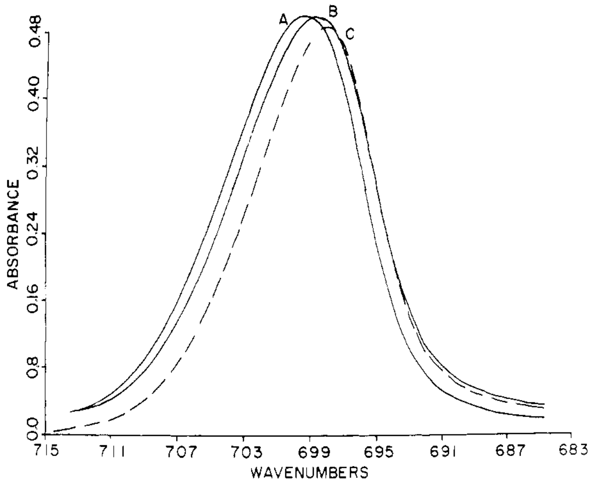

**Figure 7.** Temperature variation of 50/50 PS/PVME blends prepared from toluene solution: (A) 25 °C; (B) 70 °C; (C) 150 °C. The ordinate scale is applicable to the 25 °C spectrum.

The infrared spectra obtained for PS and the 50/50 PS/PVME blends are shown in Figures 6 and 7, respectively. Below 120 °C no significant changes were seen in either the incompatible blends cast from TCE or pure PS. However, for compatible mixtures cast from toluene (Figure 7), thermally induced spectroscopic changes differ considerably from those of either the pure components or the incompatible blends. At temperatures above LCST, temperature phase separation occurs. Therefore, the PS 700-$cm^{-1}$ band shifted continuously downward in frequency as expected. However, the frequency never reached the value of 697.7 $cm^{-1}$ found for pure PS at 150 °C. This result suggests complete phase separation did not occur, consistent with earlier results.

## Conclusions

Even though a number of questions remain regarding the use of vibrational spectroscopy to characterize the conformation and environment of individual components in polymer blends, our studies of PS/PVME systems revealed definite spectral features sensitive to compatibility. These findings initially are based on the differences found for incompatible or compatible samples prepared by varying solvents. Incompatible blends can also be prepared

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from compatible mixtures at temperatures above LCST. The spectral changes in those cases are similar to those for the different samples cast from various solvents. The molecular level of intermixing that occurs in PS/PVME blends may include dispersion forces from several chemical groups. Since the bands most sensitive to changes in compatibility are the CH out-of-plane bending of PS and the COC asymmetric stretching of PVME, among the many possibilities, interaction between the ring and the $COCH_3$ group may be influential, leading to compatibility for this pair of polymers. In this paper we gave emphasis to finding molecular spectroscopic features sensitive to compatibility. It is well-known that both thermal and mechanical properties of binary mixtures are particularly sensitive to the degree of compatibility. We have characterized the molecular response of these blends when samples are deformed macroscopically. Our results will be reported in another publication.

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**Registry No.** Polystyrene, 9003-53-6; poly(vinyl methyl ether), 9003-09-2.

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# Ferroelectric Transition in a Copolymer of Vinylidene Fluoride and Tetrafluoroethylene

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ABSTRACT: Crystallographic changes consistent with a Curie transition have been demonstrated by X-ray diffraction in an 81/19 mol % copolymer of vinylidene fluoride ($VF_2$) and tetrafluoroethylene ($F_4E$). This allows generalization of our earlier conclusions obtained from copolymers of $VF_2$ with trifluoroethylene ($F_3E$) and circumvents any uncertainties related to the role of that comonomer; these include the similarity of the paraelectric structure to that of poly(trifluoroethylene), as well as the introduction into the $PVF_2$ chain of different chemical species, tacticity defects, and regicity defects associated with $F_3E$. In contrast, the tetrafluoroethylene copolymer investigated here is equivalent to $PVF_2$ containing a slightly higher percentage of head-to-head defects. In unpoled specimens of this $F_4E$ copolymer, the ferroelectric → paraelectric transition is partly thwarted by the onset of melting, while in poled films it is almost completely aborted by melting. However, cooling from the melt causes first crystallization of the paraelectric phase and then full transformation to its ferroelectric counterpart. As in the case of $F_3E$ copolymers, the all-*trans* ferroelectric phase is transformed above the Curie transition to a paraelectric state consisting of partly disordered chains that contain TG, T$\bar{\text{G}}$, and TT sequences and that are packed in an expanded pseudohexagonal unit cell. In agreement with this disorder, single crystals of the $F_4E$ copolymer grown at high temperatures in the paraelectric phase exhibit irregular morphological features and lack crystallographic faceting; such crystals also provide indications of an unusual phenomenon—irreversible ferroelectric → paraelectric transformation induced by electron irradiation.

## Introduction

The ferroelectric behavior of poly(vinylidene fluoride) is now clearly established and has recently been reviewed.[1–4] However, a common and characteristic property of ferroelectric crystals, i.e., the existence of a Curie transition at which polarization is lost through a solid-state transformation to a paraelectric phase, is still controversial for this polymer: on the one hand, an isolated paraelectric phase has never been obtained in the ferroelectric β-phase of poly(vinylidene fluoride) [$PVF_2$], and the prior occurrence of melting at 170–185 °C has been invoked for its absence;[5,6] on the other hand, a Curie transition has been suggested around 140 °C from dielectric results,[7] while very recent X-ray data have indicated that such a transition may be commencing just below the final stages of melting in β-$PVF_2$.[8] We have obtained some insight on this topic by examining by X-ray diffraction and dielectric techniques a series of random copolymers of vinylidene fluoride ($VF_2$) and trifluoroethylene ($F_3E$);[9–11] these had previously been found to exhibit secondary DSC endotherms[12–14] that were shown to accompany solid-state transitions to a paraelectric phase.[13–16] Our results[9–11] showed that the nature of these transitions is primarily intramolecular: the ferroelectric state in copolymers containing at least 65 mol % $VF_2$ consists of molecules in an all-*trans* conformation such as that of β-$PVF_2$;[17] the paraelectric phase is very similar to that of atactic poly(trifluoroethylene),[18,19] with chains packed hexagonally and containing TG, T$\bar{\text{G}}$, and

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