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Comparison of crystalline thin poly(vinylidene (70%)–trifluoroethylene (30%)) copolymer films with short chain poly(vinylidene fluoride) films

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Comparison of crystalline thin poly(vinylidene (70%)–trifluoroethylene (30%)) copolymer films with short chain poly(vinylidene fluoride) films

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Abstract

We compare the photoemission and electron energy loss spectra of crystalline poly(vinylidene-fluoride with trifluoroethylene: 70%: 30%), P(VDF–TrFE), films, fabricated by the Langmuir–Blodgett technique and annealed in vacuum, with in situ thermally evaporated films of poly(vinylidene-fluoride) (PVDF) in vacuum. The electronic structure and vibrational modes of the short chain PVDF films compare well with the crystalline P(VDF–TrFE) films indicating that vacuum annealed films prepared ex situ are free of significant surface contamination once vacuum annealed. The electronic structure for the short chain PVDF films exhibits, however, different temperature dependence than the crystalline P(VDF–TrFE) films.

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Keywords: Ferroelectric polymers; PVDF; Photoemission; Electron energy loss

1. Introduction

Photoemission [1–6], inverse photoemission [2,3,7,8] and high resolution electron energy loss [4,6,9] spectroscopy studies have been undertaken on the crystalline surfaces of copolymer films of polyvinylidene fluoride with 30% of trifluoroethylene, P(VDF–TrFE 70:30). The experimental band structure [7,8] and band symmetries [6] of the crystalline polymer have been successfully compared with theory [10]. In addition, a surface phase transition at about 295 K [2,6–8] and a compressibility (lattice stiffening) at about 160 K [4,9], distinct from the bulk ferroelectric transition at about 350 K, are evident in these electron spectroscopies.

Since the crystalline poly(vinylidene fluoride with 30% of trifluoroethylene), P(VDF–TrFE 70 : 30), films are prepared ex situ by Langmuir–Blodgett monolayer deposition from a water subphase, then annealed in vacuum, one issue that is not directly addressed in such studies is the possibility of impurities at the surface. While scanning tunneling microscopy provides considerable evidence of long range order [7,8,11–13], as does the experimental band structure mapping [7,8], this is not compelling direct evidence of an impurity free surface layer. Impurities could include water [14] and absorbed organic species. The spectroscopic signatures of PVDF can, however, provide a benchmark of film quality, free from chemical contamination.

Comparison with evaporated short chain polymer films formed in situ by thermal evaporation provides one means for addressing the efficacy of using the very surface sensitive electron spectroscopies to crystalline P(VDF–TrFE 70: 30) films prepared ex situ. We can also address whether the electronic structure of short chain PVDF films is fundamentally different than crystalline P(VDF–TrFE 70: 30) films. The copolymer poly(vinylidene fluoride–trifluroethylene, 70: 30) has lower bulk ferroelectric phase transition critical temperature (~80 °C) than the melting

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point (~160 °C) while the critical bulk ferroelectric transition temperature of PVDF is higher than the melting point (~200 °C) [14,15].

2. Experimental and theoretical details

The very thin crystalline P(VDF–TrFE 70: 30) films were formed by Langmuir–Blodgett monolayer deposition from water subphase, as described elsewhere [15,16]. The films were prepared by gentle annealing to 150 °C in vacuo and surface composition characterized for P(VDF–TrFE 70: 30) with core level spectroscopy (XPS) and inverse photoemission (IPES) as described elsewhere [2–4,6–8]. For in situ deposition by thermal evaporation of PVDF, a commercial PVDF powder (Aldrich) was used. Although the average chain of the commercial PVDF evaporation source was quite large (approximately ~534,000 amu or about 8300 (CH2–CF2) monomers; average length of the polymer chain ~2.2 μm), nonetheless, the chain length of the evaporated PVDF was quite short. The mass spectra, taken in a magnetic sector mass spectrometer, of the heated PVDF vapor prepared by evaporation at 250 °C (Fig. 1a), and 350 °C (Fig. 1b), indicates few chains longer than 8 to 9 (CH2–CF2) monomers. On the basis of the mass spectrometer results, we undertook to fabricate our short chain PVDF films by thermal evaporation with the source at about 230°C at 1×10^{-7} Torr. The film thickness was monitored with a quartz crystal thickness monitor. The layer-to-layer packing of the film formed from evaporated PVDF was characterized by θ–2θ X-ray diffraction. The reflection for the <110> layer spacing, at about 20°, is characteristic of the crystalline copolymer P(VDF–TrFE) films [4,8,15,16] (and shown as an inset to Fig. 2). This diffraction feature is also evident for the in situ evaporated short chain polymer films, though the diffraction peak is much broader than for the films fabricated by Langmuir–Blodgett techniques, as seen in Fig. 2. The X-ray diffraction of the in situ evaporated short PVDF films also exhibits an additional diffraction peak at 22.5°, not found for the films fabricated by Langmuir–Blodgett techniques.

As both PVDF and copolymer PVDF–TrFE films are insulating, very thin samples were essential for the electron spectroscopies to avoid excessive charging of the sample surface. Therefore, nominally 2 to 5 monolayer P(VDF–TrFE 70:30) films and ~100 to 150 Å PVDF films were chosen for this work. The evaporation temperature and sample temperatures were determined using a chromel–alumel thermocouples.

For the angle-resolved photoemission studies at the Center for Advanced Microstructure and Devices (CAMD) synchrotron light facility, synchrotron radiation was dispersed by a plane-mirror grating monochromator beamline described in detail elsewhere [17]. The measurements were performed in an ultra high vacuum (UHV) chamber employing a hemispherical electron energy analyzer with an angular acceptance of ±1°, as described elsewhere [18]. The combined resolution of the electron energy analyzer and monochromator was about 0.25 eV. All angles (both light incidence angles and photoelectron emission angles) reported herein, are given with respect to the substrate surface normal. The electron energy loss spectroscopy (EELS) was undertaken using an LK-2000 spectrometer at Oak Ridge National Laboratory.

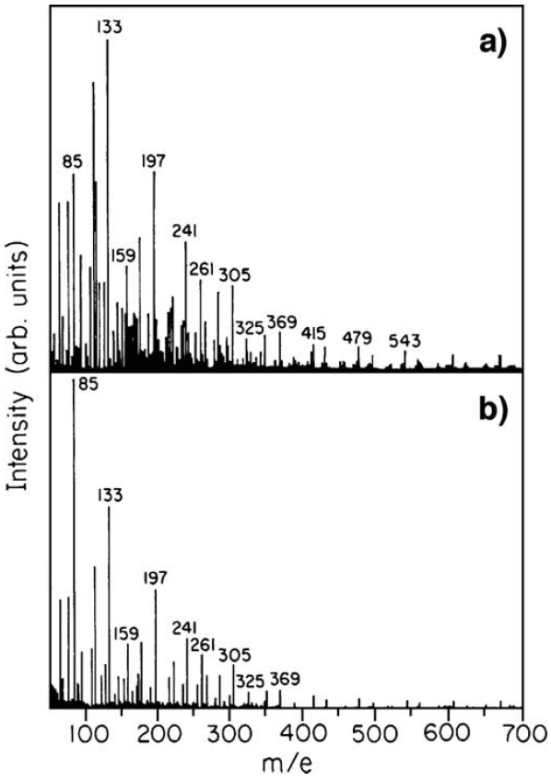


Fig. 1. Mass spectra from thermally evaporated PVDF at 350 °C (a) and 250 °C (b).

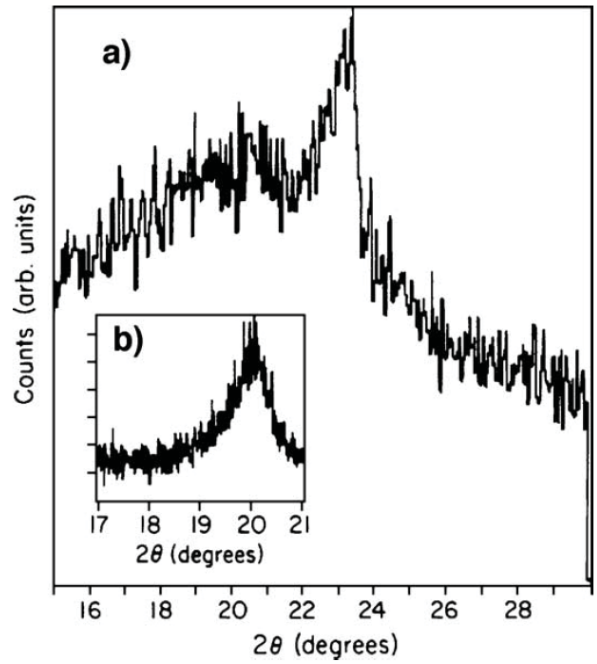


Fig. 2. X-ray diffraction spectra are taken at room temperature using Cu-Kα line for a) ~100Å thick PVDF formed by thermal evaporation, and b) a nominally 5 monolayer copolymer P(VDF–TrFE 70:30) film fabricated by the Langmuir–Blodgett technique.

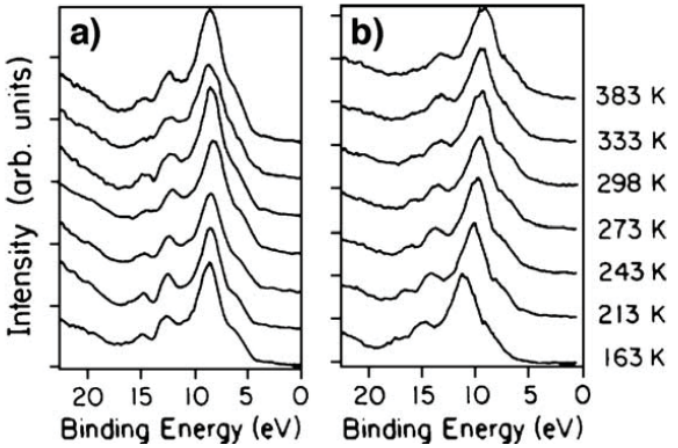


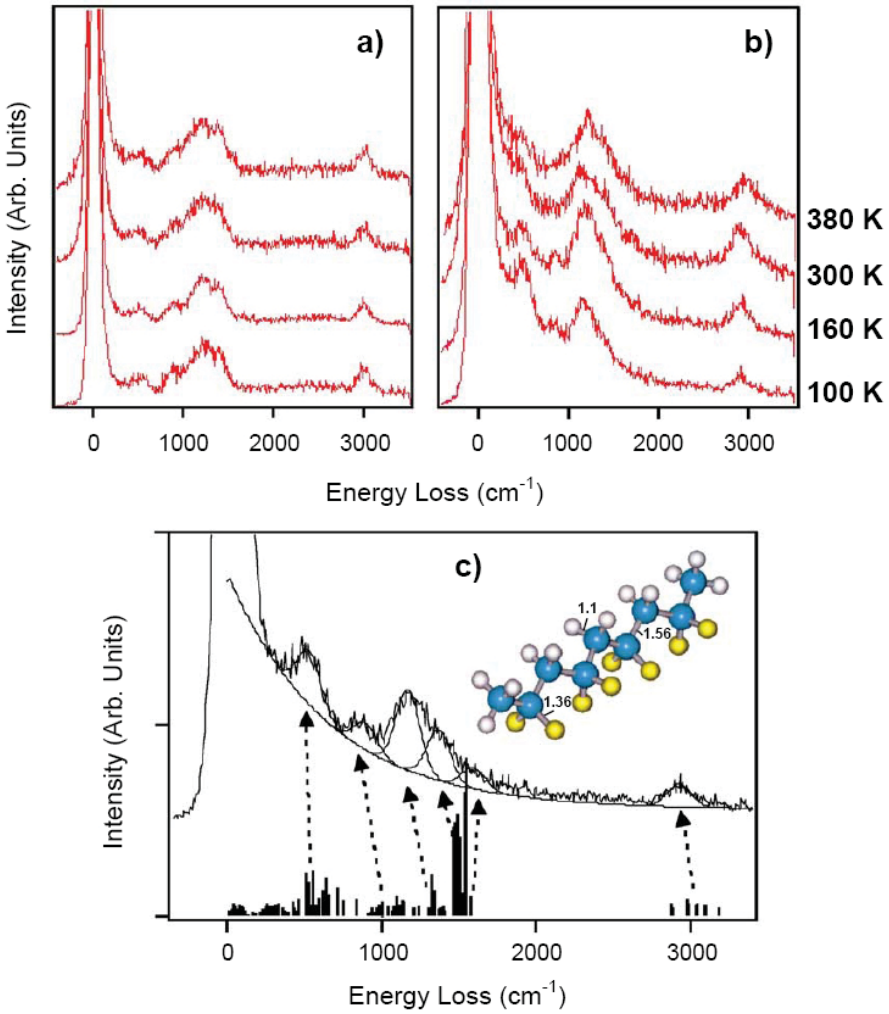
Fig. 3. Valence band photoemission spectra taken at normal emission as a function of temperature from a) a ~100 Å thick PVDF film deposited in situ by evaporation and b) nominally 5 monolayer crystalline films of P(VDF–TrFE 70: 30) films fabricated ex situ by Langmuir–Blodgett techniques. The incident photon energy is 42 eV.

The electron energy loss spectra were taken at the specular geometry as a function of temperature.

The vibrational modes determined from high resolution electron energy loss spectroscopy are compared with a semiempirical calculation for a molecule of 4 monomers of vinylidene fluoride and 2 monomers of trifluoroethylene for both the all-*trans* configuration and the alternating gauche and *trans* configuration structures. The vibrational modes were calculated with an MNDO-PM3 (modified neglect of differential overlap, parametric method 3) Hamiltonian. This Hamiltonian does not include solid state effects and dipole–dipole coupling. The geometrical structures are optimized (C_{2v} for the all-*trans* configuration and C_s for the alternating gauche and *trans* configuration) and the vibrational modes then calculated. The optimized geometrical parameters in these calculations are as follows: the bond lengths of C–C, C–F, and C–H are 1.568, 1.380, and 1.087 Å , respectively. The angles of C–C_F–C, C_F–C–C_F, H–C–H, F–C–F, C–C–F, and C–C–H are 110.3, 112.5, 108.6, 107.3, 109.9 and 108.9 in degrees, respectively, where the subscript *F* indicates a carbon atom which is bonded with a fluorine atom(s).

The vibrational modes obtained from the semi-empirical calculation were compared with the ab initio calculation derived from the Gaussian method with the STO-3G basis

Fig. 4. Electron energy loss spectra taken at the specular geometry, as a function of temperature, from a) a 150Å thick evaporated PVDF film and b) a 2 monolayer P(VDF–TrFE 70: 30) film formed by Langmuir–Blodgett techniques. The electron energy loss features for a 2 monolayer P(VDF–TrFE 70:30) film formed by Langmuir–Blodgett techniques at 100 K can be compared with semi-empirical theory as indicated (c), with the all-*trans* configuration of the copolymer in the ferroelectric phase illustrated as an inset.



set, in a fashion similar to that undertaken for adsorbed molecules elsewhere [19]. The latter ab initio calculations show a larger deviation from experiment, so we restrict the discussion here to a comparison with the semi-empirical calculations. Some differences are observed between the all-*trans* configuration and the alternating gauche and trans configuration structures, as noted elsewhere [6]. Nonetheless, the all-*trans* configuration is most applicable to the experimental results reported here and is the focus of the semi-empirical calculations reported here. This corresponds to the ferroelectric phase of the polymers, with the dipoles oriented perpendicular to the chains (along the surface normal in experiment).

3. Comparison of short chain PVDF and crystalline PVDF–TrFE Films

The photoemission from nominally 5 monolayer crystalline films of P(VDF–TrFE 70:30) films and ~100 Å evaporated films of PVDF are quite similar, as seen in Fig. 3. The valence band photoemission spectra, taken at normal emission as a function of temperature, show all the expected photoemission characteristics of crystalline films of PVDF [6]. The characteristic difference between the photoemission spectra taken from nominally 5 monolayer crystalline films of P(VDF–TrFE 70:30) films (Fig. 3b) and ~100 Å evaporated films of PVDF (Fig. 3a), is the absence of a shift towards higher binding energies with decreasing temperatures below 233 K for the short chain evaporated films of PVDF. This binding energy shift, observed for crystalline copolymer films of P(VDF–TrFE 70:30), is one of several characteristic signatures of the lattice stiffening transition (compressibility transition) observed at about 160 K [4]. The binding energy shift is possibly due to an increase in dielectric properties of the film as greater dipole ordering is established in the vicinity and at temperatures below 160 K [4].

There is also qualitative agreement between the observed vibrational modes of crystalline films of P(VDF–TrFE 70:30) films and evaporated films of short chain PVDF, as seen in Fig. 4. The electron energy loss spectra as a function of temperature, from both a nominally 2-monolayer P(VDF–TrFE 70:30) film (Fig. 4b) and a ~150 Å thick evaporated PVDF film (Fig. 4a), are quite similar. As with the photoemission spectra, there is little or no temperature dependence in the electron energy loss spectra from evaporated PVDF (Fig. 4a). For the electron energy loss spectra of crystalline copolymer P(VDF–TrFE) films, there is a large change in the electron energy loss spectra, particularly in the vicinity of the 500 cm^{-1} loss feature.

As indicated in Fig. 4c, and summarized in Table 1, the electron energy loss features can be assigned by its vibrational mode and symmetry based on our semiempirical calculations. The calculated frequencies reported here tend to be somewhat higher than measured and calculated by K. Tasihiro et al. [20]. Our calculations do not include the solid state effects, so some differences with experiment must be anticipated. The large difference between the experimental and theoretical values could come from overestimated C–C

Table 1
Comparison of vibrational modes of all-*trans* geometric structure for both PVDF and P(VDF–TrFE); vibrational modes are named as $\upsilon_{s,a}$ for symmetry or antisymmetry stretching mode, δ for bending mode, w for wagging mode, r for rocking mode, and t for twisting mode

Vibrational properties		PVDF (cm^{-1})			P(VDF–TrFE) (cm^{-1})	
Modes	Symmetry representation	MO theory	EELS	Ref. [20]	MO theory	EELS
υ_a (CH_2)	B_2	3052	2995±82	3021	3044	2922±74
υ_s (CH_2)	A_1	2985		2993	2982	
δ (CH_2)	A_1	1560	1650±82	1429	1547	1580±74
υ_a (CC)	B_1	1552		1389	1542	
w (CH_2)	B_1	1504		1389	1539	
υ_s (CF_2)	A_1	1496	1382±100	1270	1494	1360±100
υ_s (CC)	A_1	1487		1270	1469	
δ (CCC)	A_1	1477		1270	1467	
υ_a (CF_2)	B_2	1317		1180	1340	
r (CH_2)	B_2	1316	1177±100	1180	1322	1166±100
υ_a (CC)	B_1	1306		1063	1240	
t (CH_2)	A_2	1067		953	1095	
υ_a (CF_2)	B_2	1028		897	1040	
r (CH_2)	B_2	965		897	1001	
r (CF_2)	B_2	948		897	984	
υ_s (CF_2)	A_1	948	914±82	837	966	892±74
υ_s (CC)	A_1	785		837	937	
δ (CF_2)	A_1	540	524±82	504	639	526±74
w (CF_2)	B_1	528		470	560	
r (CF_2)	B_2	468		430	507	
t (CF_2)	A_2	243		255	258	

The vibrational values under MO theory are obtained by a semiempirical calculation using MNDO PM3 (modified neglect of diatomic overlap, parametric method 3).

and C–F bond lengths and underestimated H–C–H, C–C_F–C, and C_F–C–C_F bond angles.

Across the surface ferroelectric phase transition at 295 K and the lattice stiffening transition at 160 K, dipole ordering is expected [4,9], largely along the surface normal [6]. This should be reflected in increases in the electron energy loss features for the dipole active modes below these temperatures. Consistent with this picture, the bending mode of CF_2 (A_1), and rocking mode of CF_2 (B_2) both contribute to the feature at around 526 ± 74 cm^{-1} but the mode is dipole active below 295 K [6] and thus is dominated the bending mode of CF_2 (A_1). While the rocking modes of CF_2 (B_2) and CH_2 (B_2) will be expected to be observed, these are impact scattering modes with the ferroelectric dipole oriented along the surface normal [6]. The experimentally observed electron energy loss features at around 892 ± 74 cm^{-1} are seen to increase with decreasing temperature for crystalline copolymer P(VDF–TrFE 70:30) films but not for the temperature dependent electron energy loss spectra taken from evaporated PVDF, consistent with an origin to a dipole active stretching mode like $v_s(CF_2)$ of A_1 symmetry [6].

As with the photoemission spectra, the temperature dependent electronic energy loss spectra of evaporated short chain PVDF provide no indication of a surface ferroelectric phase transition nor any indication of the lattice stiffening transition observed with crystalline copolymer films of PVDF–TrFE. In many other respects the spectra are very similar, providing more direct confirmation that PVDF and copolymer PVDF–TrFE films prepared ex situ and can then be annealed under ultra high vacuum to produce surface free of contamination. We cannot address whether long chains or crystalline order are necessary for observation of the surface ferroelectric phase transition at 295 K and the lattice stiffening transition in the vicinity of 160 K, but the results here suggest that one or both may be a requirement.

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