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Substrate effects on crystallization of polyvinylidene fluoride from solution

V. GELFANDBEIN, M. M. PERLMAN
Groupe de Recherche sur les Semiconducteurs et les Diélectriques, Département de Physique, Collège Militaire Royal de Saint-Jean, Saint-Jean, Québec, Canada

Different concentrations of the α, β and γ polymorphs of polyvinylidene fluoride (PVDF) result on casting from solution onto substrates of steel, aluminium, Teflon^R, copper, gold and silicon. The polymer solution was in contact with the oxides of the metals, and with the (100) surface of the silicon monocrystals. X-ray diffraction, infrared spectroscopy, polarized optical and scanning electron microscopy show that iron and aluminium oxide substrates promote crystallization of PVDF mainly in the α form. Copper oxide and gold strongly stimulate the β form with some α form. Teflon favours the α form, and silicon the β form. Specimens cast on silicon yield a highly oriented "columnar" structure perpendicular to the film surface, and show a pyroelectric response without any previously applied electric field. Some interesting results were obtained from attempts to match the polymer–oxides and polymer–metal lattices.

1. Introduction

There are five known crystal forms of polyvinylidene fluoride (PVDF) [1–4]. Three of them, called β, γ and δ are polar, piezoelectric and pyroelectric. The β form gives the best performance when used in practical devices. The latter may be grown from solution under special conditions [5], from the melt [6], or by stretching films originally containing the α form [1, 7]. Growth from solutions such as dimethylformamide or dimethylsulphoxide usually lead to the γ form [8]. The lattice parameters of the various polymorphs of PVDF are summarized in Table I.

This paper describes preliminary results on the crystallization of different forms of PVDF from solution onto different substrates, and subsequently studied by X-ray diffraction, infrared spectroscopy, polarized optical and scanning electron (SEM) microscopy.

2. Experimental details

PVDF powder was supplied by The Aldrich Chemical Co. [9]. Cast films ~ 7 to 10 μm thick, were obtained by evaporation from a solution (of 1.5 wt% PVDF in dimethylsulphoxide at 80° C) on substrates of steel, aluminium, Teflon^R, gold, copper and silicon. The substrate surfaces were cleaned with acetone before casting. Their exact compositions are not specified here. The polymer solution was in contact with the oxides of the metals, and with the (100) surface of the silicon monocrystals. The films were annealed at 130° C for one day. A Philips X-ray diffractometer, a Perkin Elmer 627 infrared spectrometer, an Alpha 9 ISI scanning electron microscope, and optical microscopes were used in this work.

3. Results

X-ray diffraction scans of these films, taken in the reflection mode, are shown in Fig. 1. They reveal that steel, aluminium and Teflon substrates lead mainly to the α polymorph. Shoulders in the scans at 20.7° indicate the presence of a small amount of the β polymorph. The different

TABLE I PVDF lattice parameters

Form	*a* (nm)	*b* (nm)	*c* (nm)
α (II)	0.496	0.964	0.462
β (I)	0.858	0.491	0.256
γ (III)	0.497	0.966	0.918
δ (IV)	0.496	0.964	0.462

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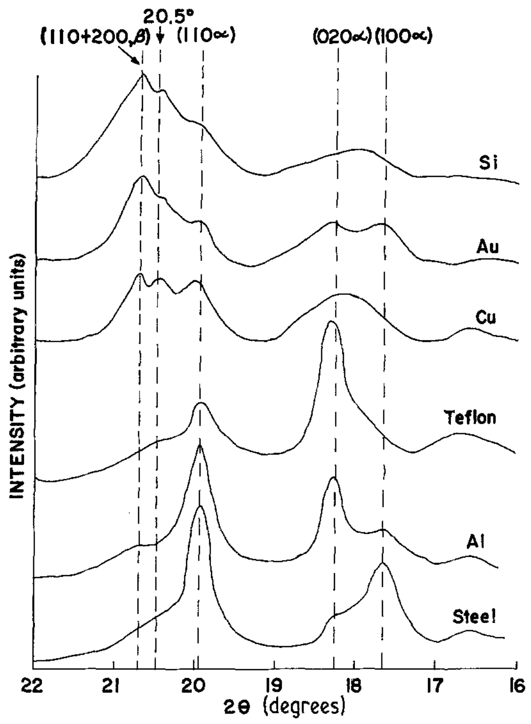


Figure 1 X-ray diffraction scans (Cu$K\alpha$ radiation) for (1.5 wt %) (PVDF) films cast from dimethylsulphoxide solution at 80° C onto different substrates.

intensities of the (110), (020) and (100) α peaks are probably due to different orientations of crystallites on the substrate surfaces. Copper and gold substrates favour crystallization in the β form, with some α. Silicon substrates result in films with small (100) and (020) α peaks, and three other closely spaced peaks at 19.9°, 20.5° and 20.7°. Those at 19.9° and 20.7° are attributed to the presence of the α and β forms, respectively. The origin of the peak at 20.5° is unclear. It may indicate the growth of a new crystal phase of PVDF [10].

Infrared (IR) spectra of films cast on steel (Fig. 2a), aluminium and Teflon confirm the presence of mainly the α form, with a small amount of β (512 cm^{-1}) and γ (1235 cm^{-1}). IR spectra of films cast on copper (Fig. 2b) show the presence of some γ, more β, and less α than steel, aluminium, and Teflon [11]. Those for films cast on silicon (Fig. 2c) show mainly β.

Typical morphology of films cast on steel, aluminium, and Teflon, seen in the transmission mode using polarized optical microscopy (Fig. 3), are well formed α spherulites. The darker areas in all three photographs are most likely the β form (or possibly "mixed" spherulites [6]). Both optical microscopy and IR show more α when casting on steel than aluminium. The dimensions of the α spherulites when casting on all metals are of the order of metal grain size. Films cast on copper (Fig. 4a) led to a roughly equal mixture of α and β. Those cast on silicon (Fig. 4b) show a small number of α spherulites dispersed within the β form.

The surface topography of the cast films can be more clearly seen in the SEM photographs of Fig. 5. Films cast on steel show mostly well formed α spherulites, while those cast on copper show spherulites coexisting with a "hill-like" structure, identified as the β form. Films cast on silicon consist mostly of the latter.

Cross-sections of films cast on silicon, obtained by SEM, are shown in Figs. 6a and b. One sees a

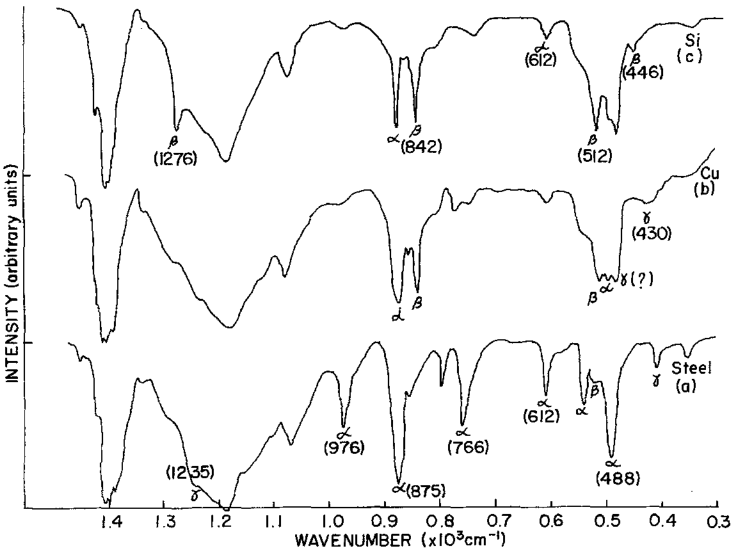


Figure 2 Infrared (IR) spectra for PVDF films cast on steel, copper and silicon.

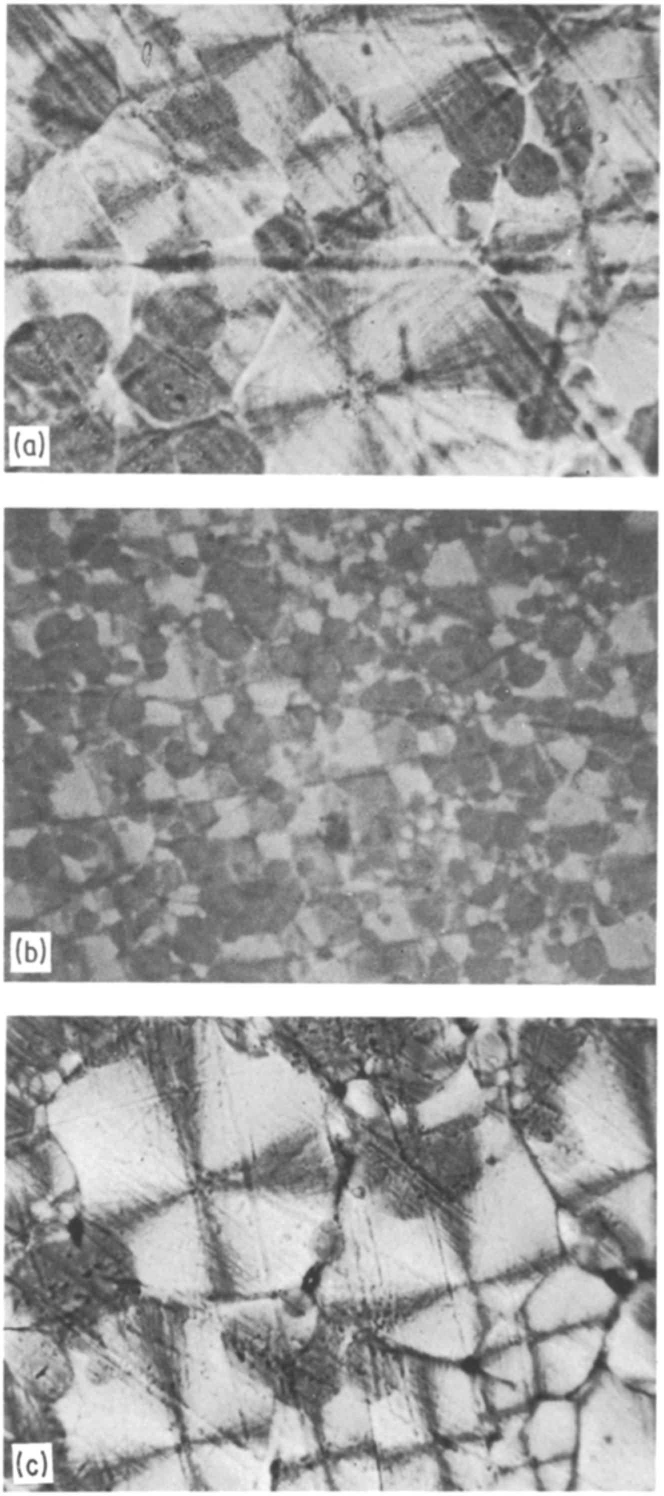


Figure 3 Polarized light optical microscopy of α spherulites and β fibrils in PVDF cast on (a) steel, (b) aluminium and (c) Teflon (275 ×).

fibril or columnar structure, strikingly oriented perpendicular to the substrate surface (Fig. 6a). The existence of these columns has been suggested previously [12]. The degree of orientation is extremely high. The fine structure is "shish-kebab"-like (Fig. 6b).

We have no direct evidence for dipole orientation perpendicular to the surface. However, if this were

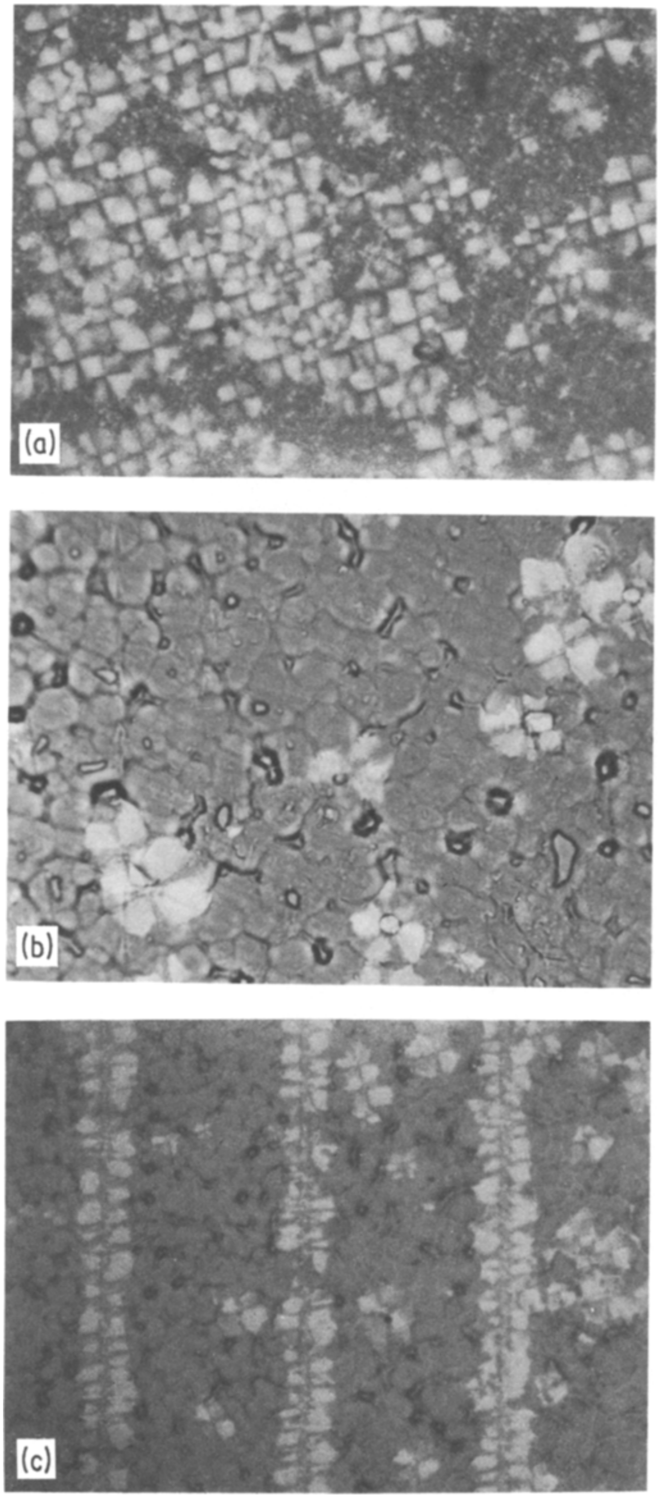
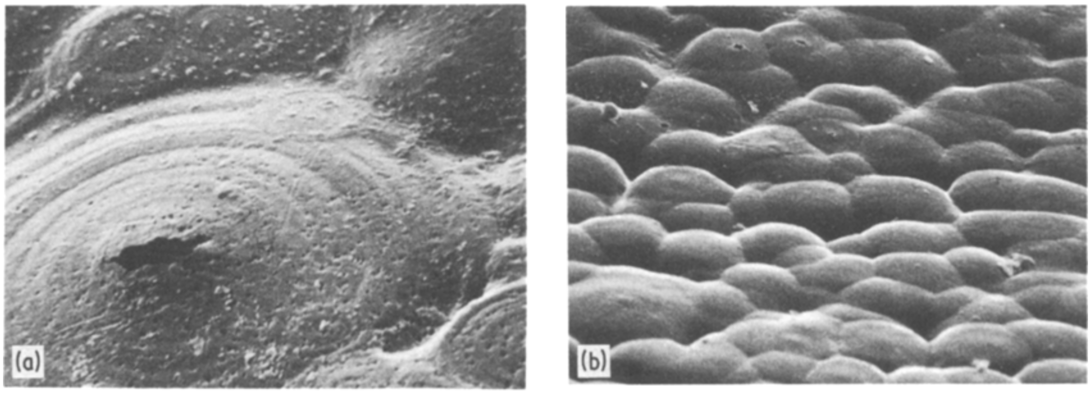


Figure 4 Polarized light optical microscopy of α spherulites and β fibrils in PVDF cast on (a) copper (275 ×), (b) silicon (275 ×) and (c) silicon plus aluminium grid (110 ×).

so, the columnar structure would be pyroelectric, without first being subjected to an applied electric field. A series of pyroelectric measurements were carried out for PVDF film cast on silicon. The experimental procedure, and the method of differentiation between the pyroelectric and irreversible discharge currents, has been described previously [13]. The pyroelectric coefficient ($p = -\mathrm{d}P/\mathrm{d}T$)



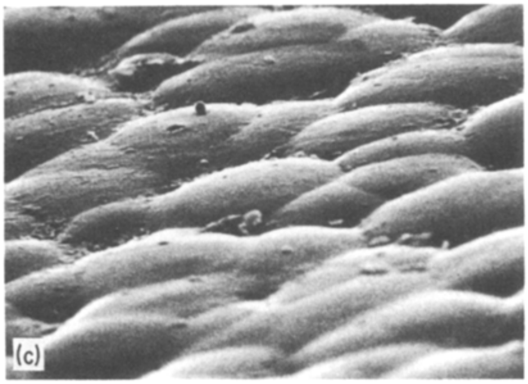


Figure 5 Scanning electron micrographs of α spherulites and β fibrils (hill-like structure) in PVDF cast on (a) steel, (b) copper and (c) silicon (800 ×).

of unpoled PVDF film, measured at room temperature, varied between -0.3 and -0.5×10^{-5} $\text{cm}^{-2}\,\text{K}^{-1}$. This is about one-fifth of that obtained for poled oriented Kureha PVDF film [14]. However, it is possible that some polarization of our film was due to charge exchange at the substrate–polymer contact during casting and annealing. Thus, it is not clear whether dipole orientation or charge exchange was responsible for the observed pyroelectric response.

Fig. 6c shows an SEM of the side of the PVDF film that was peeled from a copper substrate. While interesting, we have no explanation for the observed pattern.

4. Discussion

The growth of various crystal phases of PVDF on different substrates is analogous to epitaxial

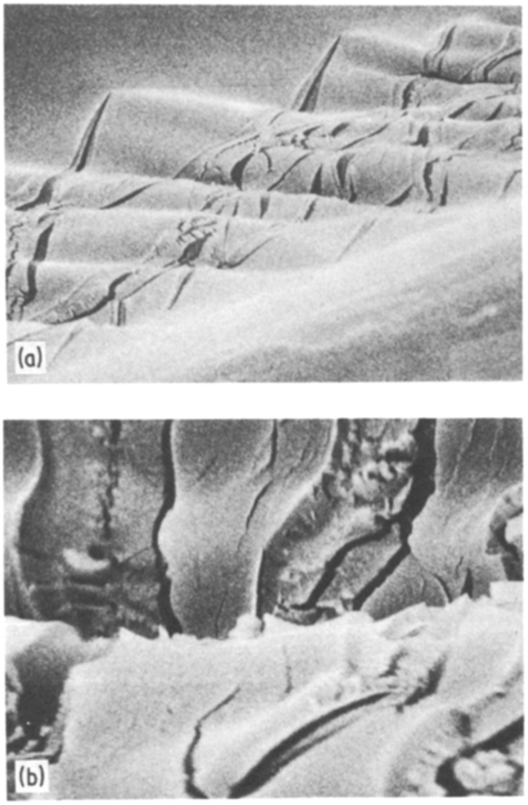
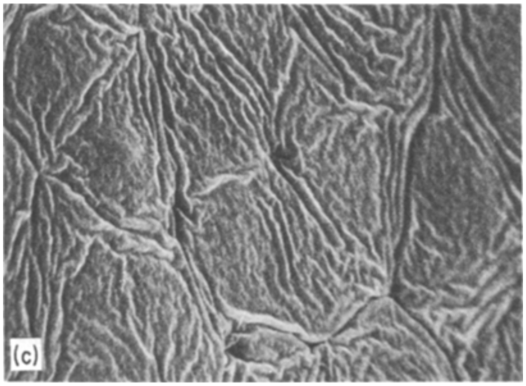


Figure 6 Scanning electron micrographs (film edge) of β fibrils in PVDF cast on silicon (a) (1600 ×), (b) (8000 ×) and (c) SEM of the side of PVDF peeled from the copper interface (4000 ×).



crystallization, as it is normally defined [15]. Although close lattice matching of polymer crystal and substrate lattices is not a necessary condition, it does promote epitaxial crystallization. Wettability of the substrate for the polymer solution is another important factor. Matching calculations for polymer–oxides and polymer–metal lattices, for various combinations of relative geometries, have been carried out. Different substrates may possess different nucleating ability for various polymer crystals, depending on relative polymer–substrate geometry. While we have some doubts about the validity of this procedure, particularly in view of the spherulitic structure of PVDF(α), some interesting results were obtained.

The mismatch in atomic spacing is usually expressed, e.g. as $(\bar{a} - \delta)/\bar{a}$, where $\bar{a}$ and δ are the lattice periodicities, in the direction of interest, of the polymer and substrate, respectively. Epitaxial growth is usually limited by a mismatch upper bound of about 15% [15].

Matching proved to be impossible for most crystallographic planes of the metal oxides, and the α, β, and γ lattices of PVDF. Only that which seemed reasonable is described below.

The most probable oxides on the metal surfaces are Fe_2O_3, Al_2O_3 and CuO. Gold is unlikely to be oxidized. The unit cell of PVDF(α) matches well on planes such as $(10\bar{1}0)$ Fe_2O_3 along the $\langle 0001 \rangle$ direction (for notation, see [16]). It is equally good on (0001) planes along the $\langle 10\bar{1}0 \rangle$ direction. Mismatches between a[PVDF(α)] or b[PVDF(β)] and a_0 for Fe_2O_3 or Al_2O_3 were all less than 3.4% (see Tables I and II). Mismatches between multiples of the c parameter of α- or β-PVDF and c_0 for the oxides were all less than 7%. The experimental results show less β for these substrates than would be expected from these calculations. Nucleation of the γ phase is less probable because c[PVDF(γ)] matches poorly to the oxides.

There is an exact match between $2c$[PVDF(β)] and c_0 of the CuO lattice. Mismatches between a[PVDF(α)] or b[PVDF(β)] and a_0 (CuO) are of the order of 5%. Thus, growth of the α and β phases are favourable when casting on copper.

The nearest neighbour distance δ in gold is 0.286 nm. An excellent match was found between a[PVDF(β)] and 3δ(Au); both were equal to 0.858 nm. The match between PVDF(α) and gold is poor (11%), but within the upper bound for epitaxy.

TABLE II Lattice parameters of various substrates

Substrate	a_0 (nm)	b_0 (nm)	c_0 (nm)
Fe_2O_3 hexagonal	0.503		1.375
Al_2O_3 hexagonal	0.479		1.299
CuO Monoclinic	0.468	0.342	0.513
Au Cubic	0.408	(nn distance is 0.286 nm)	
PTFE (at 80° C)?	0.497		

The Teflon polytetrafluoroethylene (PTFE) lattice is disordered at the casting temperature of 80° C [17]. However, X-ray diffraction spectra of the substrate showed a very strong peak, implying a lattice periodicity parameter of 0.497 nm, very close to a[PVDF(α)]. This good match promoted crystallization with the b-axis normal to the substrate surface, and gave rise to a strong (020) X-ray peak in PVDF cast on PTFE. These results agree well with these previously reported [18].

Matching calculation for casting on silicon did not agree with the experimental results.

To summarize, iron and aluminium oxide substrates promote crystallization of PVDF mainly in the α form, while copper oxide and gold strongly stimulate the β form, with the possibility of some α form. Teflon favours the α form, and silicon the β form.

An important possible application of these results is the production of polymer films with zones of different electrical activity, depending on the substrate pattern. Fig. 4c illustrates this for PVDF cast on silicon covered with an aluminium grid. The darker zones on silicon are the β form of PVDF with pyroelectric and piezoelectric properties, while the whiter areas on aluminium are α spherulites. It may prove possible to prepare solid-state electronic devices using polymer films in this manner.

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