Properties of PVDF and its copolymers.

PVDF is a semicrystalline polymer consisting of ferroelectric lamellar crystallites embedded in an amorphous dipolar matrix. Bulk PVDF is a mixture of crystalline and noncrystalline regions with a crystallinity of 50%. Its ferroelectricity was first proven by Furukawa et al. by demonstrating a hysteresis loop in the electric field dependence of the dielectric displacement, *D(E)*.[1]

The chemical structure of PVDF contains the repeat unit of doubly fluorinated ethane CH_2-CF_2. Each unit exhibits a dipole moment of 7×10^{-30} Cm associated with positively charged H-atoms opposing the negatively charged F-atoms. Since such dipoles are rigidly attached to main-chain carbons, their orientation is directly controlled by the conformation and packing of molecules. PVDF forms four polymorph crystalline phases that are defined by the conformation of the polymer chains and their steric order (crystalline structure).

The most common crystalline phase is the α-phase made up of zigzag chains composed of carbon atoms aligned in the c-axis. This varying alignment of carbon atoms is expressed by the trans-gauche conformation (TGTG’, Figure 1). PVDF molecules in trans-gauche conformation have an antiparallel packing motif (see Figure 1) in order to relax the interactions of fluorine atoms in neighbouring chains, thus resulting in a non-polar semi-crystalline material.

In the all-trans conformation (TTTT) the carbon chains are aligned in a more straight fashion (zigzag) as compared to the configuration of the α-phase. Here the CH_2-CF_2 dipoles are strictly oriented perpendicular to the chain axis (carbon nackbone). All-trans molecules prefer to be packed in a parallel fashion thus forming a crystalline structure called the β-phase. Since then the molecular dipoles in the β-phase crystal unit are entirely aligned in one direction, they generate the maximum theoretic crystalline polarization of $P_0 = 130$mC/m^2 after summing up the CH_2-CF_2 dipole moments over a unit volume.[2] By the way, the other two crystalline phases are also polar but with a much smaller spontaneous polarization than the β-phase.

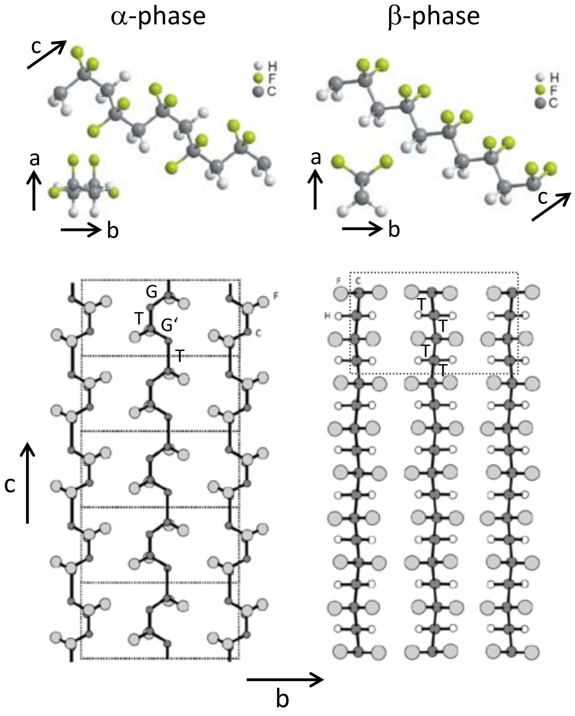

Figure 1: Chain structure of PVDF showing the TGTG’ conformation of the α-phase (left) and the TTTT conformation of the β-phase (right) observed from either parallel to c- (above) or a-axis (below). Adapted from Ref.6.

A polar structure is essential for a crystal/crystallite to be ferroelectric, however even more important is the existence of some instability in the polar structure. Accordingly, a ferroelectric material reverses its spontaneous polarization by action of an electric field and undergoes a transition into a paraelectric phase at a certain temperature, the Curie temperature. In PVDF the molecular interactions are dominated by short-range Van-der-Waals forces (over long-range Coulomb forces) with a slightly higher intramolecular contribution in the α- and a slightly higher intermolecular one in the β-phase.[3] The conversion among these polymorphs is easy since the potential barriers for the related motions (rotations of chain molecules) are very low, which is a source of instability thus facilitating not only phase transition but also polarization reversal.

PVDF melts at about $C = 170$ °C (which is below its T_c) and then directly crystallizes into the nonpolar α-phase as this one is slightly more stable than the β-phase[3]. It can be extruded in the form of plastic films, whereby mechanical drawing stretches the chain molecules and readily converts the α-phase into the all-trans polar β-phase.[2] The stretched and extruded films are quite transparent in the visible- and NIR regions (Transmission $T > 85\%$) and absorptive in the far-infrared portion of the electromagnetic spectrum.

Almost 40 years ago, it was found that the introduction of a specific amount of trifluoroethylene (TrFE, $CFH\text{-}CF_2$) into VDF induces direct crystallization into the ferroelectric β-phase from the melt. [4,5] In the copolymer VDF and TrFE units are randomly distributed along the molecular chain due to the similarity in the size of hydrogen and fluorine atoms. Furukawa et al.[2] explained that the trans bond is favoured over the gauche bond because the replacement of one hydrogen by a slightly larger fluorine atom results in steric hindrance of neighbouring G-bonds. Fujisaki[6] could show that the introduction of at least 20% of TrFE units introduces enough HH ($CF_2\text{-}CF_2$) and TT ($CH_2\text{-}CH_2$) defects to cause severe steric hindrance in an α-phase crystal but not in a β-phase one (see Figure 2). Therefore, the copolymer chains prefer all-trans conformation and then crystallize into a polar phase very similar to the β-phase of the homopolymer.

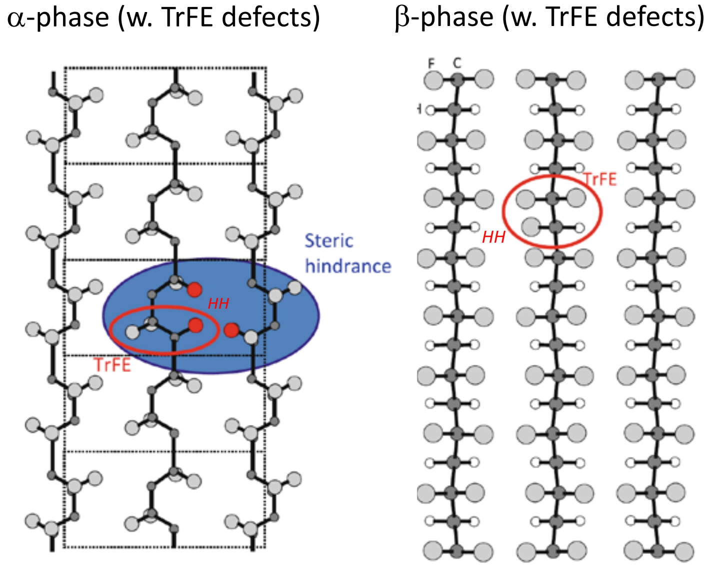
α-phase (w. TrFE defects)
β-phase (w. TrFE defects)

Figure 2: Effect of HH ($CF_2\text{-}CF_2$) defects (induced by incorporation of TrFE) on the TGTG'-conformation of the α-phase (left) as well as the TTTT-conformation of the β-phase (right). No serious steric hindrance is observed in the β-phase as opposed to the α-phase. Adapted from Ref.6

Ferroelectric and thus pyroelectric layers can be produced directly from a melt or a solution of P(VDF-TrFE), which is a major advantage when integration of such layers in technical devices is concerned. Another useful effect is the increase of crystallinity towards 90%. The incorporation of TrFE enhances the formation of crystalline regions and furthermore, by annealing the copolymer layers at temperatures in the range $T_C < T < T_m$, an increase of the crystalline domain size at the expense of noncrystalline regions is achieved.[7]

Contrary to the homopolymer PVDF (where $T_m < T_C$), the copolymers of VDF with TrFE have binary phase diagrams where the melting point T_m, the crystallization temperature T_{cr} and the ferroelectric-paraelectric phase transition temperature T_c vary smoothly with the composition, namely the ratio of VDF to TrFE. In Figure 3a the phase diagram of the P(VDF-TrFE) copolymer with T_m, T_{cr} and the Curie points upon heating $T_{c,heat}$ and cooling $T_{c,cool}$ are plotted.[11] The T_c values (circles) for the spin-on solution were determined by differential scanning calorimeter (DSC), the T_c values for samples based on a printable sol-gel copolymer (stars) were derived from the temperature dependence of its dielectric constant ε. The dielectric constant displays the ferroelectric-to-paraelectric phase transition as a distinct peak upon heating indicating the onset of cooperative dipolar motion [10] (see Figure 3b). Upon cooling re-crystallization leads to an increase of ε followed by a decrease due to the paraelectric-to-ferroelectric phase transition and a decreasing tendency to cooperative motion of dipoles with decreasing temperature (see Figure 3b).

For materials with a VDF constant above 55% $T_{c,heat} > T_{c,cool}$, which means that these transitions are first-order. At VDF ≤ 55% $T_{c,heat} \sim T_{c,cool}$ indicative of a second order transition. T_C increases monotonically with addition of VDF due mainly to an increased order of the random copolymer. T_{cr} dips to a minimum at about 80-85% VDF, so only at VDF ≤ 85% a Curie point can be observed.[8,9,12]

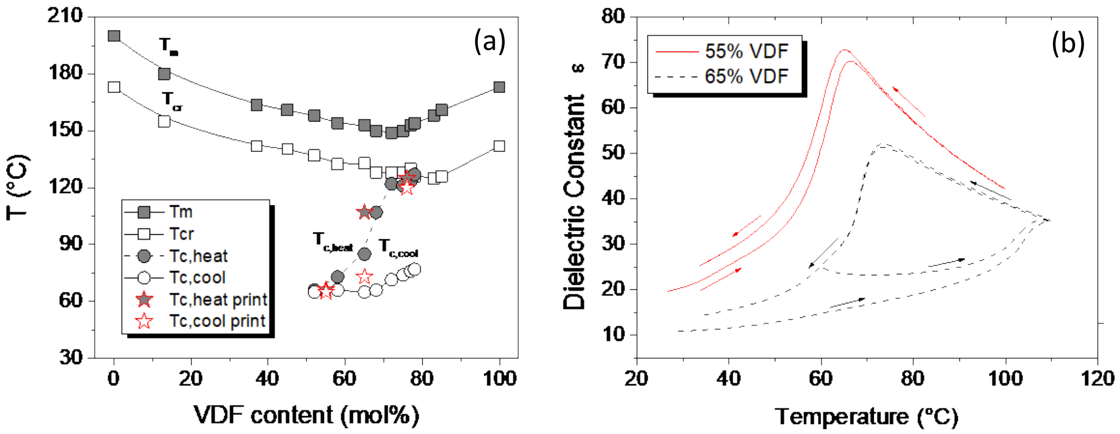

Figure 3: (a) Phase diagram for a VDF-TrFE copolymer with data from Furukawa et al. [11] showing melting temperature T_m, crystallisation temperature T_{cr}, Curie temperature upon heating $T_{c,heat}$ and Curie temperature upon cooling $T_{c,cool}$. The data were derived from DSC measurements. In addition, T_c values as derived from the temperature dependence of the dielectric constant of printable copolymer solutions are also plotted in the diagram.[10] (b) Dielectric constant ε vs. temperature of samples from a printable PVDF-TrFE solution.[10] The arrows indicate the direction of the temperature sweeps: the solid tail belongs to the first, the dashed tail to the second cycle.

Due to the increased crystallinity for PVDF-TrFE a larger remnant polarization than for the homopolymer is expected. The remnant polarization P_r is the amount of polarization that is exclusively due to the ferroelectric polarization excluding any dielectric contribution. It is determined by measuring the hysteresis loop in D(E) from which the displacement at $E = 0$ is extracted as P_r; e.g. in Figure 4a the hysteresis loops for a 5.5 μm thick screen-printed P(VDF-TrFE) layer with 70 mol% VDF reveal a $P_r = 65\ \mu C/m^2K$. The coercive field is the field at which polarization reversal is observed, it is determined as the intersection of the loop with the abscissa.

In Figure 4b the composition dependence of the remanent polarization of differently fabricated PVDF-TrFE layers is shown, it has a humpback form. The gradual increase of P_r as VDF increases from 50% to 80 mol% is attributed to an increase in the average copolymer dipole moment because the dipole moment of a TrFE unit is half that of a VDF unit. As the VDF content falls below 50 mol%, P_r decreases rapidly due to a loss of ferroelectricity. On the other hand, the decrease in P_r in the 80-100 mol% range is attributed to a decrease in the crystallinity. Homopolymer PVDF with 50% crystallinity has a remnant polarization of $P_{r,PVDF} = 65\ mC/m^2$ and a pyroelectric coefficient of $p = -25\ \mu C/m^2K$. In contrast, for copolymer PVDF-TrFE with 80 mol% VDF, resulting in a ferroelectric layer with a crystallinity of 90%, the highest remnant polarization of $P_{r,PVDF\text{-}TrFE} = 95\ mC/m^2$ and a pyroelectric coefficient $p \sim -30\ \mu C/m^2K$ is observed (Figure 4b).[11]

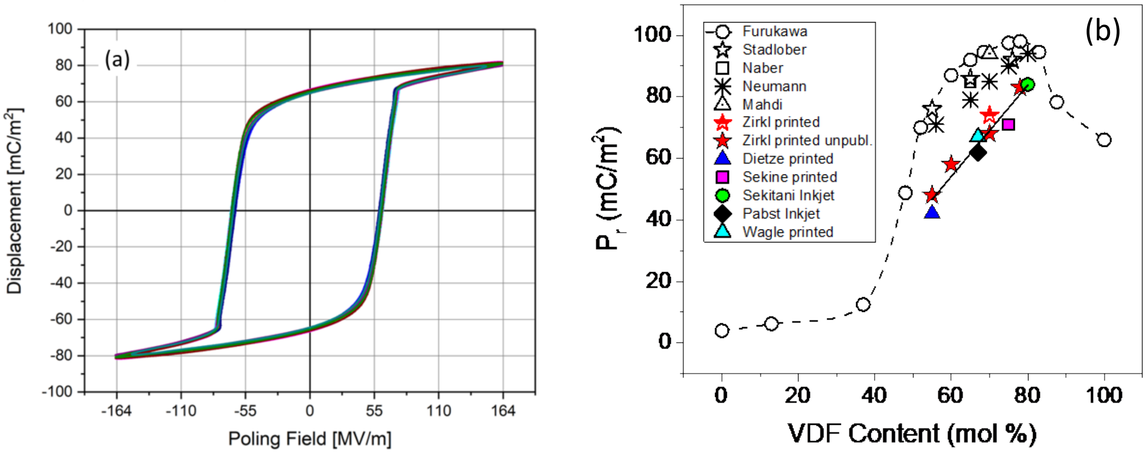

Figure 4: (a) Hysteresis loop measurement of the displacement D(E) for a screen printed 3.65 μm thick P(VDF-TrFE) copolymer layer with 70 mol% VDF content. A sine electric field E was applied at 10 Hz with peak-to-peak amplitudes of 164 V/μm. The remnant polarization P_r is equivalent to D at zero electric field. The coercive field E_c where polarization switching occurs is defined as the field at vanishing displacement.(b) Dependence of the remanent polarization of P(VDF – TrFE) copolymers on the VDF content. The P_r values for spin-on copolamer layers are taken from the following references: Furukawa[11], Stadlober[12], Naber[13], Neumann[14], and Mahdi[15]. The values collected by Furukawa are the largest ever reported in literature, the dotted line is a guideline for the eye. The P_r values for screen-printed P(VDF-TrFE) layers are taken from Zirkl[16] (incl. also unpublished data), Dietzsche[17], Wagle [18] and Sekine[19]. The values or inkjet-printed copolymers are taken from Sekitani[20] and Pabst[21]. The compact line is a linear fit for P_r values of printed layer.

Furukawa[22] reported a strictly linear relationship of the pyroelectric coefficient with the remnant polarization for a number of different P(VDF-TrFE) compositions with a larger slope for samples with higher VDF constant. It was found by several authors [22,23] that only a certain part (< 50%) of the total pyroelectricity can be attributed to secondary pyroelectricity (dimensional change). Accordingly, an important contribution to the pyroelectric coefficient in PVDF materials comes from the primary effect originating from a reversible temperature dependence of its crystallinity or, equivalently, from temperature-dependent conformational disorder.[24] For example, P_r gradually decreases with increasing temperature and then suddenly drops at T_c, its slope being equivalent to the pyroelectric coefficient p, so p develops a peak near T_c similar as does the dielectric constant. This is as a result of the competition of the cooperative force to align dipoles and the entropy force to randomize them and is more pronounced in materials with lower crystallinity.

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