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Published in:
Nature Materials

DOI:
10.1038/NMAT3577

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2013

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Revisiting the δ-phase of poly(vinylidene fluoride) for solution-processed ferroelectric thin films

Mengyuan Li1*, Harry J. Wondergem2, Mark-Jan Spijkman1, Kamal Asadi2, Ilias Katsouras1, Paul W. M. Blom1,3 and Dago M. de Leeuw1,3

Ferroelectric poly(vinylidene-fluoride) (PVDF) has, in the past, been proposed as an ideal candidate for data storage applications as it exhibits a bistable, remanent, polarization that can repeatedly be switched by an electric field. However, fabrication of smooth ferroelectric PVDF thin films, as required for microelectronic applications, is a long-standing problem. At present, the copolymer of PVDF with trifluoroethylene P(VDF–TrFE) is used, but the stack integrity and the limited thermal stability of its remanent polarization hamper large-scale integration. Here we show that smooth neat PVDF films can be made at elevated substrate temperature. On applying a short electrical pulse the ferroelectric polar δ-phase is formed, an overlooked polymorph of PVDF proposed 30 years ago, but never experimentally verified. The remanent polarization and coercive field are comparable to those of the copolymer. The enhanced thermal stability of the polarization is directly related to the high Curie temperature, whereas the ferroelectric properties are related to the molecular packing as derived from the refined crystal structure. The replacement of P(VDF–TrFE) by the commodity polymer PVDF may boost large-scale industrial applications.

PVDF (–CH2–CF2–)n is a semi-crystalline polymer with at least four different polymorphs referred to as the α, β, γ and δ-phases, previously called in order of their discovery form II, I, III and IV, respectively. Their crystal structures and phase transitions were thoroughly investigated in the 1970s and 1980s and were reviewed in a seminal book in 1995. Thermodynamically, the most stable phase at ambient temperature and pressure is the α-phase. Owing to the centro-symmetric symmetry of the unit cell, the α-phase is non-polar and paraelectric. At high mechanical deformation the phase PVDF is thermodynamically more stable than α-PVDF (ref. 3). The unit cell of β-PVDF has a macroscopic dipole moment rendering it ferroelectric. Thicker paraelectric α-PVDF films can be converted into free-standing ferroelectric β-PVDF films by biaxial stretching. The polymer chains in γ-PVDF have a conformation in between that of the α and β-phases. The γ-phase is ferroelectric but experimentally hardly achievable. Formation typically requires extreme temperature control and high pressures, although recently, γ-phase PVDF has been reported by melt re-crystallization using surface-energy-controlled top layers. The δ-phase is a polar version of the α-phase. Its existence was proposed 30 years ago by electro-forming from an originally α-phase bulk sample in a high electric field of about 170 MV m−1 (ref. 5). Although δ-PVDF is ferroelectric, hysteresis loops with values for coercive field and remanent polarization have to our knowledge never been reported.

Free-standing ferroelectric PVDF films are commercially available. However, fabrication of thin ferroelectric PVDF films, as required for microelectronic applications, is a challenge. It has been reported that highly polar solvents can induce the polar β or γ-phase in PVDF films, but this seems to occur only in micrometre-thick films, and the fraction of the polar phase strongly depends on the solvent evaporation rate. Moreover, good ferroelectric properties are usually not achieved. The fraction of β-phase can be enhanced by adding small amounts of an ionic liquid or by blending with polymethylmethacrylate.

All investigations on thin ferroelectric neat PVDF films were basically discontinued when the random copolymer P(VDF–TrFE) was reported. This copolymer is highly soluble in common organic solvents and can easily be processed into thin films that become ferroelectric on annealing close to the crystallization temperature. However, large-scale integration is hampered by the limited thermal stability of the remanent polarization due to its low Curie temperature. Furthermore, the thermal annealing causes crystal growth and an increase in surface roughness, leading to high leakage currents and a diminished reliability of ferroelectric microelectronic devices. Hence, a reinvestigation of neat ferroelectric PVDF thin films is worthwhile.

Here we show that by using elevated substrate temperatures, remarkably smooth PVDF films can easily be made. By applying a short electrical pulse the ferroelectric polar δ-phase is formed. The remanent polarization and coercive field are comparable to those of β-PVDF and of P(VDF–TrFE). To prove the formation of δ-PVDF we performed grazing-incidence X-ray diffraction (GI-XRD) and Fourier-transform infrared spectroscopy (FTIR) measurements on the same capacitors before and after electro-forming. For the interpretation of the GI-XRD measurements we reinvestigated the crystal structure of δ-PVDF. The ferroelectric properties are related to the molecular packing.

Thin-film capacitors were made by wire-bar coating and spin-coating. They behaved qualitatively the same. The crucial parameter is the substrate temperature, as it determines the film roughness. Films deposited at low substrate temperatures exhibit a high roughness. In particular, spin-coated films are extremely rough; the root-mean-squared (r.m.s.) roughness is comparable to the layer thickness. Hence, capacitors of as-cast films at room temperature are shorted. Ultrasmooth films, however, are obtained at elevated substrate temperatures. Thin films of about 400 nm, deposited at 100 °C, exhibit a r.m.s. roughness of less than 10 nm. The roughness is reduced by suppression of the PVDF crystallization...
Figure 1 | Ferroelectricity of δ-PVDF thin-film capacitors. The displaced charge density is presented as a function of applied electric field. a, Hysteresis loops during poling by stepwise increase of bias. The full hysteresis loop with a constant remanent polarization is obtained at an electric field of about 250 MV m\(^{-1}\). b, Hysteresis loops for the same thin-film capacitor after poling. The inner unsaturated loops, measured on increasing the electric field, are indicated by the red lines. The fully saturated curves are indicated in blue. The remanent polarization, \(P_r\), the displaced charge density at zero bias, amounts to 7 \(\mu C\ cm^{-2}\) and the coercive field, \(E_c\) to 115 MV m\(^{-1}\).

by faster evaporation of the solvent, here N,N'-dimethylformamide, and by a smaller driving force, the difference between substrate and crystallization temperatures.

All films both as-deposited and after further heat treatment were paraelectric. However, all samples became ferroelectric after applying a high electric field of about 250 MV m\(^{-1}\). This value agrees with that reported for making δ-PVDF from free-standing α-PVDF films using a field of 170 MV m\(^{-1}\) (ref. 5). We note that application of higher electric fields did result in breakdown of the top electrode, before dielectric breakdown of the PVDF could be observed. To obtain ferroelectricity only a short pulse train was required. Typically, a forming time of one second at a frequency of 100 Hz is sufficient to obtain a saturated hysteresis loop. After forming, the ferroelectric properties for a given capacitor were fixed. They did not change on application of a subsequent, second poling pulse.

The full set of hysteresis loops for a typical thin-film capacitor during forming is shown in Fig. 1a where the displaced charge density is presented as a function of electric field. We start from a pristine film. At low bias the capacitor is paraelectric. Then the electric field is stepwise increased. Hysteresis starts to appear and the remanent polarization increases with bias. The full hysteresis loop with a constant remanent polarization is obtained at an electric field of about 250 MV m\(^{-1}\). However, the shape is atypical; the inner loops extend beyond the fully formed outer loop. The origin is that the ferroelectric phase is being formed during the measurement. Similar atypical hysteresis loops have been reported, for neat PVDF films at high electric field, which might indicate formation of δ-PVDF (ref. 13).

The inner and outer polarization loops after forming are presented in Fig. 1b. We start with an electric field much lower than the coercive field. Only the linear dielectric polarization contributes to the displacement. On increasing the maximum applied electric field up to the coercive field, \(E_c\), the inner displacement loops start to show hysteresis (red lines). The ferroelectric polarization increases with maximum electric field, until the polarization and the hysteresis loop saturate (blue lines). The remanent polarization, \(P_r\), the displaced charge density at zero bias, amounts to 7 \(\mu C\ cm^{-2}\) and the coercive field to 115 MV m\(^{-1}\).

The polarization is comparable to that of \(\beta\)-PVDF and of the copolymer P(VDF-TrFE). The coercive field, however, is higher than both \(\beta\)-PVDF (ref. 14; about 90 MV m\(^{-1}\)) and the copolymer P(VDF-TrFE) (ref. 15; 60 MV m\(^{-1}\)).

The remanent polarization and coercive field are presented as a function of temperature in Fig. 2. The polarization increases and the coercive field decreases with temperature. Above 120 °C leakage currents prevent accurate determination of the polarization. The commonly used ferroelectric in thin-film applications is the copolymer P(VDF-TrFE). However, owing to its low Curie temperature, the polarization decreases notably already at 50 °C and rapidly deteriorates at even higher temperatures. In contrast, the polarization of δ-PVDF is stable at high temperatures, because the Curie temperature of δ-PVDF is much higher than that of the copolymer, estimated as 172 °C (ref. 16), even higher than the melting temperature of 166 °C. Finally, we note that the polarization is stable with time. As shown in the inset of Fig. 2, data retention was measured up to a week and no significant changes were found. The programming cycle endurance is presented as well. No fatigue after 10\(^6\) cycles was observed.

We note that organic ferroelectrics can be used in a wide range of applications such as touch control, piezo and pyroelectric detectors, transducers, actuators in Braille displays, non-volatile memories and energy harvesting\(^{17–20}\). Several reviews summarize the work on sensors and photonic, piezoelectric and pyroelectric applications\(^{21–23}\). We propose non-volatile memories for data storage applications. In Supplementary Section S7 we show a ferroelectric field-effect transistor and a dual gate ferroelectric transistor based on δ-PVDF, which behave as non-volatile memories. They can be programmed at voltages exceeding the coercive field and read-out non-destructively at lower biases. We note that the relatively high value of the coercive field of the organic ferroelectrics of about 100 MV m\(^{-1}\) stems from the large-scale rotation of the individual macromolecules on polarization.

Figure 2 | Temperature budget. Remanent polarization, \(P_r\) (blue), and the corresponding coercive field, \(E_c\) (red), as a function of temperature. The dashed lines are a guide to the eye. There is only a small change up to a temperature of 400 K. The thermal stability is due to the high Curie temperature of δ-PVDF. The inset shows the capacitor layout, programming cycle endurance and data retention as measured during about a week.
transformation from \(\alpha\)-PVDF into \(\delta\)-PVDF by reorientation of the polymer chains, but the applied field does not lead to crystal growth.

To prove the formation of \(\delta\)-PVDF we refined the crystal structure. The macromolecules can rotate about each single bond (Fig. 3a,b). Depending on the orientation of the substituents, two main torsional bond arrangements can be distinguished: trans(1), with a 180° orientation, and gauche(2), with a ±120° orientation. The chain conformation is \(tg\) for both the \(\alpha\)-phase and the \(\delta\)-phase. This conformation results in a dipole moment for each macromolecule with components both parallel and perpendicular to the polymer chain. The packing in the unit cell determines the value of the macroscopic dipole moment.

The crystal structures and molecular packing of \(\alpha\)-PVDF and \(\delta\)-PVDF are presented in Fig. 3. For \(\alpha\)-PVDF we used a structure proposed in ref. 26 and later refined in refs 27,28. The reported space group is \(P2_1/c(14)\). The crystal structure of \(\delta\)-PVDF was first proposed in ref. 29. We slightly adjusted the atomic positions of \(\delta\)-PVDF to equalize the chain conformations of the two phases. The space group \(P2_1/cn(33)\) is used to emphasize the similarities between the \(\alpha\) and \(\delta\) polymorphic PVDF phases. The non-standard setting of the \(P2_1/cn\) space group can be converted to the standard \(Pna2_1\) setting by exchanging the \(x\) and \(z\) values of the atomic positions and the \(a\) and \(c\) unit-cell axes. The resulting atomic positions and unit-cell dimensions are identical for both phases and are presented in Table 1. The \(\delta\)-PVDF structure is truly orthorhombic. The \(\alpha\)-PVDF structure, however, is monoclinic, on the basis of the symmetry of the structure, even though all unit-cell angles are 90°.

Table 1 | Atomic positions for both \(\alpha\)-PVDF and \(\delta\)-PVDF.

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.331</td>
<td>0.193</td>
<td>0.211</td>
</tr>
<tr>
<td>C2</td>
<td>0.230</td>
<td>0.184</td>
<td>0.897</td>
</tr>
<tr>
<td>F1</td>
<td>0.592</td>
<td>0.170</td>
<td>0.155</td>
</tr>
<tr>
<td>F2</td>
<td>0.237</td>
<td>0.078</td>
<td>0.339</td>
</tr>
<tr>
<td>H1</td>
<td>0.010</td>
<td>0.381</td>
<td>0.893</td>
</tr>
<tr>
<td>H2</td>
<td>0.309</td>
<td>0.091</td>
<td>0.793</td>
</tr>
</tbody>
</table>

\(x\), \(y\), and \(z\) are the fractions of the unit-cell axes \(a\), \(b\), and \(c\). The unit-cell dimensions are identical for both phases. The lattice constants are \(a = 4.96\) \(\text{Å}\), \(b = 9.64\) \(\text{Å}\), and \(c = 4.62\) \(\text{Å}\), and the angles between them are \(\alpha = \beta = \gamma = 90°\). The \(\delta\)-PVDF structure is truly orthorhombic. The \(\alpha\)-PVDF structure, however, is monoclinic, on the basis of the symmetry of the structure, even though all unit-cell angles are 90°.

Figure 3 | Molecular packing and crystal structure. a,b. Schematic packing of two polymer chains with the \(tg\) configuration in the unit cell of the \(\alpha\)-phase and the \(\delta\)-phase. The symbols present the in- and out-of-plane components of the dipole moment. In the \(\alpha\)-phase all contributions cancel out. In the \(\delta\)-phase the in-plane components cancel out but the out-of-plane ones yield a net microscopic dipole moment. c,d. The crystal structures and molecular packing of \(\alpha\)-PVDF and \(\delta\)-PVDF viewed along the \(c\) axis. The polymer chain is projected onto the \(ab\)-plane. e,f. Crystal structure of \(\alpha\)-PVDF and \(\delta\)-PVDF viewed along the \(a\) axis. The drawn inner lines represent the unit cells. Grey circles represent carbon atoms, red circles fluorine atoms and blue circles hydrogen atoms. The atomic positions are calculated using the atomic coordinates in Table 1.

reversal\(^{15}\). To obtain low-voltage operation, thin ferroelectric films are required. In Supplementary Section S4 we have reduced the film thickness to about 100 nm with a concomitant linear reduction of coercive voltage. The films are extremely smooth; the roughness is less than 2 nm. The remanent polarization does not depend on layer thickness and amounts to 7 \(\mu\)C cm\(^{-2}\). For the copolymer even ultrathin films have been obtained\(^{24,25}\). For \(\delta\)-PVDF thermal annealing is not needed; the phase is formed by electropoling. Fabrication of ultrathin films should be feasible.

To optimize the processing conditions we deliberately varied the molecular weight of the PVDF, the deposition temperature and the heat treatment. The ferroelectric properties did not depend on the molecular weight of the PVDF, which was varied between 180, 275 and 534 kg mol\(^{-1}\). The properties deteriorate on further heat treatment. At present the highest polarization and the lowest coercive field are obtained for films cast at 100°C and subsequently electro-formed.

Atomic force microscopy (AFM) measurements and optical micrographs showed that the as-cast films contain small spherulites of 10 \(\mu\)m, typical for microcrystalline \(\alpha\)-PVDF (Supplementary Fig. S1). We note that the microstructure does not change on electro-forming. The applied electric field induces a transformation from \(\alpha\)-PVDF into \(\delta\)-PVDF by reorientation of the polymer chains, but the applied field does not lead to crystal growth.
the drawing. In each chain, all of the C–F bonds slant either to the left or to the right. The centre of symmetry of α-PVDF requires that this direction alternates. From top to bottom in Fig. 3e the direction of the single polymer chains alternates to the left and to the right. Irrespective of the rotation mechanism, the left–right orientation of the chains will be conserved. Hence, the alternating left–right orientation of the chains in α-PVDF will also be present in δ-PVDF. We note that a statistical packing for α-PVDF has been previously proposed; details are discussed in Supplementary Section S5.

The calculated X-ray diagrams for defect-free α-PVDF and δ-PVDF (more specifically αc−PVDF) are presented in Fig. 4a. For these calculated diagrams an arbitrary large peak width was used to mimic the large peak widths experimentally found in thin films. The identical single-cell dimensions result in identical peak positions for both phases; the difference in symmetry of the space group results in differences in peak intensities. The (h k l) Miller indices are indicated. In situ experimentally observed X-ray spectra before and after electro-forming.

To experimentally prove the formation of δ-PVDF we performed GI-XRD and FTIR measurements on functional PVDF capacitors. Palladium (Pd) was used as a bottom electrode and poly(3,4-ethylenedioxythiophene) poly(styrenesulphonate) (PEDOT:PSS) was used as a top electrode because the amorphous PEDOT:PSS hardly scatters X-rays. Spectra of PVDF could then be recorded before and after electro-forming. The GI-XRD measurements can exclude the formation of β-PVDF. The FTIR measurements can exclude the formation of γ-PVDF.

The pristine film is paraelectric and the GI-XRD diffraction patterns for defect-free α-PVDF and δ-PVDF are similar. First, the calculated subtle differences are only in the peak intensities, which in thin films are strongly influenced by a preferred orientation. Second, unambiguous phase identification is hampered by the large width of the diffraction peaks. The width is large because PVDF is semi-crystalline; about half of the material is amorphous. The crystalline domains in PVDF are small and subdivided into even smaller antiphase domains, as shown previously, which leads to a further peak broadening. Finally, the differences between the two phases are calculated for defect-free PVDF. It is, however, known that the average PVDF chain has about 5% of the monomers reversed, meaning that a carbon atom with two fluorine atoms is sometimes followed by another carbon with two fluorine atoms. These head-to-tail defects are only one monomer long but have a strong influence on the crystal structure. At sufficiently high concentration these defects can even make the β-phase more stable than the α-phase.

The phase identification is corroborated by FTIR measurements on the same capacitor. The absorption was first measured on the pristine film. Then the PEDOT:PSS top electrode was applied. The film was electro-formed as checked by polarization measurements. Subsequently, the top electrode was washed away. The FTIR spectra before and after electro-forming are presented in Fig. 5. The presence of γ-PVDF can be excluded; the characteristic bands at 812, 833 and 1117 cm−1 are missing. The peak positions can be ascribed to α-PVDF (ref. 36). The same absorptions are obtained for δ-PVDF, as reported earlier for thick films. The only difference is in the far-infrared where at 73 cm−1 and at liquid-nitrogen temperature a weak new band was observed. To summarize the phase identification, pristine PVDF films crystallize in the α-phase. After electro-forming, GI-XRD measurements show no signature of β-PVDF and FTIR measurements show no signature of γ-PVDF. The electro-formed films are ferroelectric, which unambiguously proves that δ-PVDF is formed.

To validate the values for P, and E, derived, we estimate the remanent polarization and compare the coercive field of δ-PVDF with that of β-PVDF. The remanent polarization scales in first-order approximation with the dipole moment and the crystallinity. The dipole moment per monomeric unit is a function of chain length because the dipole moment in an individual unit is perpendicular to the chain and the chain is curved. The dipole moment for an α-chain and β-chain has been calculated using density functional theory. For a length of 20 monomeric units, values of $4 \times 10^{-30}$ C m and $5 \times 10^{-30}$ C m, respectively, the pristine sample. However, the film became ferroelectric, which implies that the film is δ-PVDF.

It is not surprising that the experimental diffraction spectra are similar. First, the calculated subtle differences are only in the peak intensities, which in thin films are strongly influenced by a preferred orientation. Second, unambiguous phase identification is hampered by the large width of the diffraction peaks. The width is large because PVDF is semi-crystalline; about half of the material is amorphous. The crystalline domains in PVDF are small and subdivided into even smaller antiphase domains, as shown previously, which leads to a further peak broadening. Finally, the differences between the two phases are calculated for defect-free PVDF. It is, however, known that the average PVDF chain has about 5% of the monomers reversed, meaning that a carbon atom with two fluorine atoms is sometimes followed by another carbon with two fluorine atoms. These head-to-tail defects are only one monomer long but have a strong influence on the crystal structure. At sufficiently high concentration these defects can even make the β-phase more stable than the α-phase.

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To validate the values for $P_r$ and $E_c$, derived, we estimate the remanent polarization and compare the coercive field of δ-PVDF with that of β-PVDF. The remanent polarization scales in first-order approximation with the dipole moment and the crystallinity. The dipole moment per monomeric unit is a function of chain length because the dipole moment in an individual unit is perpendicular to the chain and the chain is curved. The dipole moment for an α-chain and β-chain has been calculated using density functional theory. For a length of 20 monomeric units, values of $4 \times 10^{-30}$ C m and $5 \times 10^{-30}$ C m, respectively.
are obtained. Assuming the same crystallinity of about 50%, a remanent polarization for δ-PVDF of 5.6 μC cm⁻² is expected, in good agreement with the experimentally determined value of about 7 μC cm⁻². We note that during ferroelectric switching only chains perpendicular to the applied electric field can be rotated and can therefore contribute to the remanent polarization. The X-ray diffractograms of Fig. 4b show that the largest intensities are obtained for the (h k 0) reflections. This implies a textured film where most of the chains are lying in the plane of the substrate, which explains the relatively high remanent polarization obtained. Furthermore, electro-ferroforming of δ-PVDF from α-PVDF requires not only rotation of chains, but also a translation over half the c-axis lattice constant. In contrast, ferroelectric switching involves only rotation of the polymer chains. Hence, the poling field is much higher than the coercive field, as shown in Fig. 1. The coercive field of δ-PVDF determined as 115 MV m⁻¹ is comparable to that of β-PVDF of typically 90 MV m⁻¹. Similar values are expected as the dipole moments and the rigidity of the main chains are comparable.

Smooth PVDF thin films can be made at elevated temperatures. As-deposited films, irrespective of the molecular weight of PVDF, crystallize in the non-polar α-phase and comprising capacitors are paraelectric. However, all films become ferroelectric on electro-forming by applying a short pulse of about 250 MV m⁻¹. Then ferroelectric δ-PVDF, or more appropriately, polar α₁,α₂-PVDF is formed out of non-polar α-PVDF. The phase identification is corroborated by combined GI-XRD and FTIR measurements on pristine and electro-formed capacitors. The similarity in the crystal structure and molecular packing of δ-PVDF and α-PVDF polymorphs is discussed and related to the ferroelectric properties. The main difference between the two polymorphs might be in the temperature dependence of the α₁- relaxation as measured by dielectric spectroscopy and presented in Supplementary Section S6. For films as-deposited at 100 °C, without any further processing, a remanent polarization of up to 7 μC cm⁻² and a coercive field of 115 MV m⁻¹ have been determined. These values are comparable to those of δ-PVDF and of the copolymer PVDF-TrFE. The high thermal stability is due to the high Curie temperature of δ-PVDF. The limited number of reports on δ-PVDF might be due to the delicate processing. High substrate temperatures and electro-forming are required to obtain smooth films. The data show that neat PVDF is a worthwhile candidate for roll-to-roll processing of ferroelectric microelectronic devices.

Methods

Experimental details are presented in Supplementary Section S2. Thin PVDF films of about 400 nm were fabricated from a solution in N,N-dimethylformamide by wire-bar coating (Meyer rod) and spin-coating. The substrate temperature was varied between room temperature and 140 °C. The morphology of the films was characterized by AFM and to ascertain the crystal phase of the films, both GI-XRD and FTIR were used. Capacitors were fabricated on thermally oxidized silicon mirror wafers on which 50-nm-thick Au or Pd bottom electrodes were photolithographically defined. After film deposition, the capacitors were finished by evaporating a Au top electrode through a shadow mask. To allow phase identification with GI-XRD, large device areas of 1 cm² were fabricated without strongly diffracting Au top electrodes. An amorphous conducting polymer PEDOT:PSS, a water-based suspension of poly(3,4-ethylendioxythiophene) stabilized with poly(4-styrenesulphonic acid), was used instead. Electric displacement loops versus electric field for the capacitors were measured using a Sawyer–Tower circuit. Dielectric spectra were measured using an impedance gain phase analyser.

Received 29 October 2012; accepted 28 January 2013; published online 17 March 2013

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Acknowledgements

We would like to acknowledge T. Geuns for technical assistance, R. Beerends for AFM measurements, R. Bakker (all from Philips Innovation Services) for FTIR measurements and J. van Turnhout (Technical University of Delft) for discussions on dielectric spectroscopy. We acknowledge A. Marrani (Solvay) for supply of the ferroelectric polymers, and J. Michels (TNO, Holst Centre) and N. Stingelin (Imperial College, London) for fruitful discussions. We acknowledge B. Noheda for making the ferroelectricity measurement set-up available. We acknowledge A. van Breemen and B. van der Putten (TNO, Holst Centre) for a-GIZO substrates. We acknowledge financial support by the Zernike Institute for Advanced Materials, and by the EC Program (FP7/2007-2013) under grant Agreement No. 248092 of the MOMA Project.

Author contributions

M.L., M.S. and I.K. fabricated the structures and carried out the measurements. H.J.W. refined the crystal structure. All authors contributed to the preparation of the manuscript.

Competing financial interests

The authors declare no competing financial interests.