Polymer 54 (2013) 5330-5337

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Direct stamping and capillary flow patterning of solution processable piezoelectric polyvinylidene fluoride films



polyme

Weili Ong^a, Cangming Ke^a, Pin Lim^a, Amit Kumar^b, Kaiyang Zeng^b, Ghim Wei Ho^{a,*}

^a Department of Electrical and Computer Engineering, Faculty of Engineering, National University of Singapore, Singapore 119260, Singapore ^b Department of Mechanical Engineering, Faculty of Engineering, National University of Singapore, Singapore 117576, Singapore

ARTICLE INFO

Article history: Received 2 April 2013 Received in revised form 16 July 2013 Accepted 23 July 2013 Available online 31 July 2013

Keywords: Polyvinylidene fluoride Piezoelectricity Patterning

ABSTRACT

It is well known that the potential applications of polyvinylidene fluoride (PVDF) mainly come from the piezoelectricity and ferroelectricity of its polar β phase. Thus, we have investigated the effect of different preparation conditions namely evaporation temperature, type of solvent and additive to enhance the β crystal structures of PVDF thin film. Subsequently, facile and direct soft lithography technique; direct stamping and capillary flow were employed to demonstrate good pattern transfer of PVDF thin films. The piezoelectricity of the microstructure was characterized using piezoresponse force microscopy (PFM) where fairly good piezoresponse was obtained without further processing procedures i.e., annealing or applied pressure/electric field. As such, our solution processable and direct patterning of PVDF techniques offer facile and promising route to produce arrays of isolated microstructures with improved piezoelectric functionality.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

PVDF (polyvinylidene fluoride) is one of the semicrystalline polymers with its polymorphism characteristics of possessing four crystalline phases known for its pyroelectric, piezoelectric and ferroelectric properties [1–5]. PVDF exhibits different crystal phases largely depending on the processing and crystallization conditions. These different crystal structures include nonpolar orthorhombic α -phase, polar orthorhombic β -phase, monoclinic γ phase, and δ -phase [6]. The most readily available α -phase, which has trans-gauche TGTG conformation is usually obtained from melt crystallization at atmospheric pressure whilst δ -phase can be obtained by polarizing α -phase with high electric field. On the other hand, γ -phase is usually obtained from high temperature crystallization with conformation intermediate of α - and β -phases [6]. Though α -phase being the most easily and commonly formed, the β-phase is the most highly sought among other crystals phase since it has all trans planar zigzag configuration (TTT) with enhanced pyro and piezoelectric properties. The β -phase is typically obtained by mechanical deformation of melt-crystallized films [6]. Other works which have successfully obtain β -phase PVDF include the molecular epitaxy on the surface of potassium bromide [7] crystallization at high pressures [8] and drawing of ultrathin PVDF films

0032-3861/\$ - see front matter © 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.polymer.2013.07.062 prepared by melt blending [9]. However, these are not facile processes and some of which are arduous or not compatible to thin film processes. Furthermore, for the interest of large scale and practical thin film application, it is important to tune various polymorphs based on inexpensive and facile solution process with controlled and reproducible conditions.

Other than the processing conditions to tune the various polymorphs, patterned PVDF micro and nanostructures have attracted a great deal of interest for high density electronic, multiferroics, energy harvester, and microelectromechanical systems (MEMS) applications. Various techniques have been employed to pattern ferroelectric micro and nanostructures which include electron/ionbeam writing, self-assembling, nanoimprint and soft lithography [10–18]. While electron/ion-beam writing are able to pattern uniform arrays of nanostructures, the high processing cost, low throughput, and structural defects induced by the high energy ion/ electron beam may alter/degrade the polarization in ferroelectric materials. On the other hand, though self-assembling of ferroelectrics molecules is an inexpensive process, precise control of patterned nanostructures over large-scale is often difficult to achieve. In recent years, soft lithography has emerged as promising techniques for fabricating functional nanostructures. Soft lithography involves pattern transfer with low cost, high throughput and fairly high resolution well-suited for large scale practical applications. The underlying pattern transfer mechanisms can either involve mechanical stamping of inking solution or chemical-



^{*} Corresponding author. Tel.: +65 65168121; fax: +65 67754710. *E-mail address:* elehgw@nus.edu.sg (G.W. Ho).

physical processes between the elastomeric molds and capillary flow solution.

Here, we have investigated the effects of different preparation conditions namely evaporation temperature, type of solvent and additive on enhancement of β crystal structures of PVDF thin film. Subsequently, we employed facile direct stamping and capillary flow techniques to demonstrate the patterning of PVDF thin films. The piezoelectricity of the microstructure was characterized using PFM (Piezoresponse Force Microscope) where fairly good piezoresponse was obtained without further processing such as annealing or applied pressure/electric field, usually required for PVDF polymers processed from solution. Our method is beneficial since direct or one step printing or capillary flow produced isolated ferroelectric patterns without carrying out any harsh post processing which tend to degrade the functional properties of ferroelectrics.

2. Experimental details

2.1. Preparation of PVDF thin films

The organic solvents used were N, N-dimethylformamide (DMF) and mixed solvent of DMF and acetone (volume ratio 1:1). The PVDF powder (molecular weight $M_w \sim 534,000$) was dissolved in the organic solvents at 1–5 wt%. To completely dissolve the PVDF powder, the solution was heated at 50 °C in a water bath for 1 h. The precursor solution was kept at room temperature for sufficient time (12 h) to reach thermal equilibrium. The PVDF films were deposited by spin-coating the precursor onto silicon wafers at 1000 rpm for 30 s and dried at 25–100 °C for 1 h. As for the study on the effect of additive, 2 and 4 wt% of magnesium nitrate hexahydrate, Mg(NO₃)₂·6H₂O was added to the PVDF solutions followed by similar process as described earlier.

2.2. Preparation of pattern mold

Silicon wafer was cleaned in ethanol and isopropyl alcohol (IPA) ultrasonic baths sequentially to remove the organic contaminations. Positive photoresist S1805 was coated onto the substrate by spin-coating at 3000 rpm for 50 s followed by post-baking at 115 °C for 1 min. Exposure of the photoresist was conducted using a UV light source through a chrome mask for an exposure duration of 10-12 s. The developer used for the photoresist was MF319. The fabricated photoresist mold was used for stamping process.

In addition, the photoresist mold was used as template for Polydimethylsiloxane (PDMS) casting without additional pretreatment. PDMS stamp was fabricated using Sylgard 184 silicone elastomer mixed with a curing agent (Dow Corning, USA) at a ratio of 10:1 by weight. The silicone elastomer mixture was then cast on a photoresist patterned Si master and evacuated in a vacuum jar. It was maintained at a pressure of 10^{-1} Torr for 20 min. This is to ensure that any trapped air bubbles were effectively removed. Finally, it was cured in a conventional oven at 60 °C for 24 h and the PDMS stamp was peeled off from the master. After the curing process, the PDMS mold was separated from the photoresist mold and used for capillary flow soft lithography patterning. All the patterning was carried out using PVDF of 2–3 wt % with DMFacetone mixture.

2.3. Characterisation of PVDF

To determine the crystal structure of the as-prepared PVDF films, the X-ray diffraction patterns (XRD) were conducted (D8-ADVANCE, Bruker AXS GmbH, Karlsruhe). Fourier transform infrared (FTIR) spectra of the thin films were obtained from FTIR spectroscopy (Spectrum 2000, Perkin–Elmer) using reflectance

mode. Scanning electron microscopy (SEM) was used to observe the surface morphology of the PVDF films. The thicknesses of the films were determined from the SEM images of the cross section view. To study the piezoelectric effect of the as-prepared PVDF thin films or patterned PVDF, the samples were examined by PFM (MFP-3D, Asylum Research, Santa Barbara, CA, USA) for surface topographies and polarization characteristics under biased-voltage.

3. Results and discussions

The formation of PVDF crystalline structures and their surface morphologies depend on several factors which include organic solvent used, drying temperature of the spin-coated film and the addition of metal hydrates. The mixture of different α , γ and β crystals phase formation is dependent on the solvents used. DMF and acetone are used in this work since polar solvents usually give rise to thin films with dominantly β crystals [19]. It is important that PVDF of dominant ferroelectric β crystals is obtained in which parallel packing of all trans chains in an orthorhombic unit cell synchronizes chain rotation of the consecutive transconfiguration, i.e., TTTT sequence. β crystal provides the best polarization among other polymorphic crystalline structures of α and γ with the configurations of TGT-G and TTTG respectively [20]. The effect of solvent on the PVDF surface morphology was examined. Typical PVDF film surfaces resulting from the spin casting was observed to be rough and porous. From the SEM images of Fig. 1, it is evident that DMF-acetone solvent yields a less porous PVDF films than that when using the DMF solvent. It has been observed that DMF-acetone is good solvent of PVDF as such complete dissolution of PVDF with clearer solution can be obtained before spin coating. It is known that evaporation temperature is another important factor since it not only affects the structure of the films but also influences the piezoelectric functional properties [20]. Thus, other than the solvent, the effect of evaporation temperature (25 and 100 °C) on the PVDF thin film surface morphology was also studied. It is observed that in general low evaporation temperature results in grainy and porous films.

Fig. 2a presents the FTIR results for the PVDF thin films prepared under different conditions namely different solvents and evaporation temperatures. The dash lines on the graphs indicate the theoretical positions of the characteristic bands for each phase of PVDF. The characteristic absorption bands of α -phase PVDF are around 795 cm⁻¹, and bands of β -phase PVDF are around 840, 1275 cm⁻¹ [20,21]. The γ -phase has an absorption band around 1233 cm⁻¹ [22]. The relative amplitude of each peak indicates the amount of the phase presented in the PVDF thin film. From the transmission spectra, it can be seen that β phase is predominantly formed in the thin films that employed the use of DMF-acetone mixture solvent. PVDF film that are processed using high polar solvents will crystallize with the polar groups that tend to rotate the strong dipoles of the C–F bond in the PVDF molecular chain, and hence reduces the energy barrier for formation of expanded β all-trans conformation [19]. XRD spectra (Fig. 2b) were also obtained which show consistent result as the FTIR measurements where the use of DMF-acetone mixture solvent promotes β phase formation. It is observed that evaporation temperature also has an effect on the phase formation among the thin films prepared using the mixture of DMF-acetone solvent. The thin films dried at 25 °C shows enhanced β -phase compared to those dried at 100 °C. This is consistent with other report that the resulting crystalline phase depends on the crystallization rate, which in turn is determined by the evaporation rate of the solvent [20]. Low evaporation rates favor the formation of the trans-planar β phase. It is also noted that solvent evaporated at higher temperature of 100 °C exhibits enhanced α -phase peaks as such higher solvent evaporation temperature favors predominant trans-gauche α phase [20].



Fig. 1. SEM images of PVDF films using different solvent and temperature (a) DMF at 25 °C (b) DMF at 100 °C (c) DMF-acetone at 25 °C and (d) DMF-acetone at 100 °C.



Fig. 2. (a) Transmission spectra and (b) XRD spectra of various PVDF films based on different temperature and solvent. (DA denotes DMF and acetone solvent, D denotes DMF solvent). (c) Film thickness versus wt% PVDF concentrations.

The relation between film thickness and the precursor concentration was determined in order to facilitate the stamping process. The thicknesses of the films were determined from the cross section SEM images of the films. Different film thicknesses were plotted with the variation of wt % concentration of PVDF as shown in Fig. 2c. Films obtained from 2 to 3 wt % concentration of PVDF precursor with thicknesses of 1.3–1.7 μ m will be used for stamping patterning since it is observed that the PVDF film obtained at 1 wt % concentration of PVDF precursor is porous and hence not used for patterning.

Next, the effect of hydrated salt additive on resultant PVDF film is examined for both morphology and crystal phase. It has been reported that addition of hydrated salt promotes β phase formation [19,23]. SEM images in Fig. 3a show the surface morphologies of PVDF with DMF-acetone solvent thin films after the addition of 4 wt% Mg(NO₃)₂·6H₂O. Small irregular shaped Mg hydrated salts particles diameter of 50-400 nm can be observed with the addition of $Mg(NO_3)_2 \cdot 6H_2O$. These particles are uniformly dispersed across the PVDF thin film. Fig. 3b shows the EDX obtained from the PVDF films with and without the addition of $Mg(NO_3)_2 \cdot 6H_2O$ on Si substrates. The EDX spectra clearly show Mg element is detected for samples with additives with the presence of hydrated salts particles while only F, C and Si elements are detected from the samples without additives. The effect of adding Mg(NO₃)₂·6H₂O into precursor solutions with DMF-acetone solvent was examined using FTIR (Fig. 3c). The FTIR results indicate that the addition of Mg(NO₃)₂·6H₂O increases the amount of β -phase PVDF as evident from the increasing intensity of the 840 cm^{-1} band. The broad band at \sim 3400 cm⁻¹ can be attributed to the stretching of the OH group in crystalline Mg hydrates [19]. The crystal structures of the films were also confirmed by the XRD as shown in Fig. 3d. Typical diffraction peak of the β phase (110) at 20.8° is observed to increase with the addition of $Mg(NO_3)_2 \cdot 6H_2O$. The water molecules of the hydrated salt possess bond angles and bond lengths similar to the CH₂ group of PVDF [6]. Hence, the water molecules and adjacent

PVDF chains form hydrogen bonds at the interface of hydrated salt and PVDF [19]. These bonds formation result in the registration of fluorine atoms and enhance *trans* conformation in the PVDF polymer chain [19].

Two methods of PVDF patterning were attempted namely soft lithography using elastomeric PDMS molds as capillary flow channels and stamping. In particular, micromolding process driven by capillary force can be one of the most facile ways of patterning polymer solutions, under the condition that organic solvent does not swell or dissolve PDMS mold. Flexible PDMS stamp is used for the micromolding by capillary force since it has many attributes to offer which include (i) low cost and easy replication from original master structure, (ii) gas permeability for the evaporation of organic solvents during the patterning process, (iii) easy demolding process and less sensitivity to the contaminants on sample surface due to its flexibility [24]. In the capillary flow method, the PDMS mold were cleaned with ethanol and brought into conformal contact to clean Si. Next, liquid PVDF of 2-3 wt % with DMF-acetone mixture was flowed at the inlets of the PDMS channels with syringe. Through capillary force, the PVDF precursor was drawn into the mold. The substrate and the mold were then evaporated on hotplate at 25 °C for 1 h before peeling back the mold. PDMS has a relatively low surface energy, hence PVDF preferentially adhered to the Si substrate. The process flow is illustrated in Fig. 4a. Different amount of PVDF (\sim 0.3, 1.0, 2.0 and 3.0 µL/min) were injected into the 2 µm width PDMS channels. The resultant PVDF patterns on Si substrates are shown in Fig. 4b-e. Essentially, directional drying of PVDF solution has resulted in line patterning of PVDF film. Samples flow with 0.3 and 1.0 uL/min PVDF solution shows irregular and rough edge line patterns (Fig. 4b-c). On the other hand, the line patterns for sample with 2.0-3.0 µL/min PVDF solution are observed to be relatively well-defined (Fig. 4d-e). However, it is noted that as the PVDF solution increased to 3.0 µL/min, over filling of PDMS channels and spillage of PVDF solution resulted in alternate residual and patterned PVDF lines.



Fig. 3. SEM images of PVDF thin films with the addition of (a) 4 wt % of Mg(NO₃)₂.6H₂O. Inset show higher magnifications image. (b) EDX, (c) FTIR transmittance and (d) XRD spectra of PVDF with and without the addition of Mg(NO₃)₂.6H₂O.



Fig. 4. (a) Schematics process flow of printing PVDF patterns using capillary flow method based on PVDF of 2–3 wt % with DMF-acetone mixture. (b–e) Various line patterns printed with increasing amount of PVDF flow volumes.

The other PVDF patterning method utilizes a photoresist or PDMS stamping mold where PVDF of 2–3 wt % with DMF-acetone mixture was spin-coated. PDMS/Si mold coated with PVDF solution was stamped onto substrate before peeling back. The process flow which results in the final product is shown in Fig. 5a. SEM images are taken on the stamping mold at different magnifications (Fig. 5b–c). It is observed that a periodic pattern of the stamping mold has a width of 2 μ m and pitch of 4 μ m. Fig. 5c–d show the patterned PVDF that has been transferred to PDMS substrate. The patterning of PVDF using stamping mold transfers the original patterns but with slightly modified line width. This may be due to slight compression of the stamping mold on the PDMS which resulted in the expansion of the line width. In general, both direct patterning of PVDF techniques, stamping and capillary flow are able to offer a facile route to transfer isolated nano/microstructures with insignificant PVDF residue.

For device applications of PVDF microstructures, it is important to characterize the piezoelectricity properties of the PVDF patterns using PFM. Topography images of three-dimensional (3D) and twodimensional (2D) topographies of the PVDF patterned lines are shown in Fig. 6a–b. The patterned lines show width of ~2.8 μ m and periodicity of ~4 μ m which are printed using capillary flow



Fig. 5. (a) Schematics process flow of printing PVDF patterns using photoresist mold. SEM images of (b-c) photoresist molds and (d-e) transferred pattern lines on PDMS substrates based on PVDF of 2–3 wt % with DMF-acetone mixture.

method. The 3D topography image shows the height of the PVDF pattern \sim 300 nm. The cross-section of the pattern line has a trapezoidal shape where the edge of the line pattern is slightly raised to a height of \sim 380 nm while the center of the pattern line is relatively flatter and lower (height of \sim 300 nm). The resultant cross-sectional geometry may be due to incomplete filling of PVDF solutions and wetting characteristics of the PDMS stamp surface with the PVDF polymeric solution. The edge of the line pattern is dominated by the capillary force at the interface between the

solution and the stamp, while the center of the line pattern is dictated by the gravitational force on the solution.

Fig. 6c–d show the PFM amplitude and phase images of the patterned PVDF lines, which clearly show the piezoresponse of the capillary flowed patterned PVDF microstructure. In this case, an AC voltage is applied to the PVDF pattern through a conductive AFM tip to induce surface vibration. The tip is driven near the contact resonance of the tip-specimen system by applied AC voltage to magnify signal and the piezoresponse is detected through the



Fig. 6. PFM results of capillary flowed PVDF line patterns (a) 3D topography (b) 2D topography (c) PFM amplitude and (d) phase.

vibration of AFM cantilever in contact with the PVDF. From the PFM amplitude image represented by color scale bar in picometers (Fig. 6c), it is observed that the highest PFM amplitude is approximately 90 pm under an ac modulation voltage of 2.2 V. This result

is obtained on the PVDF line patterns, confirming the piezoelectricity of the patterned PVDF microstructure instead of the substrate. This is a reasonable piezoresponse of a PVDF microstructure unpolarized by an electric field. Furthermore, there is excellent



Fig. 7. PFM mean amplitude response, amplitude and phase images of various capillary flowed PVDF films (a-c) bulk and (d-f) 2 µm line patterns.

correlation between the PFM amplitude and phase image. On the PVDF line pattern, the PFM phase image is rather uniform, suggesting a uniform distribution of polarization without obvious domain divisions. Away from the line patterns, PFM amplitude shows insignificant response confirming that isolated microstructures without residue PVDF are patterned. The absence or minima PVDF residue on unpattern areas is critical for direct patterning without going through any post processing especially for the area of the high performance electronics applications.

Fig. 7a–c and d–f show the mean amplitude response, amplitude and phase images of various PVDF films, both bulk and line pattern respectively. The effective d_{zz} value can be obtained from the gradient of amplitude response versus applied voltage plot, as such bulk PVDF sample (Fig. 7a) is ~ 10.62 pm/V. On the other hand, the amplitude response of the 2 µm lines (Fig. 7c) exhibits a higher response than that of the bulk sample. The effective d_{zz} value was determined to be ~ 16.02 pm/V. It is observed that the piezoresponse of PVDF film increase with decrease in feature size possibly due to increase confined crystallization of the patterned PVDF films which can induce some degrees of PVDF polymer chains alignment resulting in enhanced piezoelectric β phase [25,26]. Similarly, there is excellent correlation between the PFM amplitude and phase images for both bulk and line patterns PVDF films.

4. Conclusion

We have demonstrated the effect of processing conditions i.e., solvent, evaporation temperature and addition of Mg hydrated salt on the phase transformation of PVDF thin film. Predominantly β -phase ferroelectric PVDF films are deposited using optimized conditions. Low cost and facile soft lithography Printing and capillary flow methods have been shown to produce PVDF micropatterns with fairly good pattern transfer between the molds and films. The line patterns exhibit piezoresponses which are seen to correlate with the line width of the patterns as such they increase with the decrease in feature sizes.

Acknowledgment

This work is supported by the National Research Foundation R-263-000-A27-281 (under NRF2011 – CRP 001-057).

References

- Omote K, Ohigashi H. Temperature dependence of elastic, dielectric, and piezoelectric properties of "single crystalline" films of vinylidene fluoride trifluoroethylene copolymer. J Appl Phys 1997;81:2760–70.
- [2] Zhao XZ, Bharti V, Zhang QM, Romotowski T, Tito F, Ting R. Electromechanical properties of electrostrictive poly(vinylidene fluoride-trifluoroethylene) copolymer. Appl Phys Lett 1998;73:2054–6.

- [3] Furukawa T. Piezoelectricity and pyroelectricity in polymers. IEEE Trans Electr Insul 1989;24:375–93.
- [4] Chan HL, Zhao Z, Kwok KW, Choy CL, Alquie C, Boue C, et al. Polarization of thick polyvinylidene fluoride/trifluoroethylene copolymer films. J Appl Phys 1996;80:3982–92.
- [5] McFee JH, Bergman Jr JG, Crane GR. Pyroelectric and non linear optical properties of poled polyvinylidene fluoride films. Ferroelectrics 1972;3: 305.
- [6] Hasegawa R, Takahashi Y, Chatani Y, Tadokoro H. Crystal structures of three crystalline forms of poly(vinylidene fluoride). Polym J 1972;3:600.
- [7] Lovinger AJ. Crystallization of the β phase of poly(vinylidene fluoride) from the melt. Polymer 1981;22:412–3.
- [8] Schenbeim J, Nakafuku B, Newman BA, Pae KD. High-pressure crystallization of poly(vinylidene fluoride). J Appl Phys 1979;50:4399–405.
- [9] Wang J, Li H, Liu J, Duan Y, Jiang S, Yan S. On the α→β transition of carboncoated highly oriented PVDF ultrathin film induced by melt recrystallization. J Am Chem Soc 2003;125:1496–7.
- [10] Ferris JH, Li DB, Kalinin SV, Bonnell DA. Nanoscale domain patterning of lead zirconate titanate materials using electron beams. Appl Phys Lett 2004;84: 774–6.
- [11] Hong S, Klug JA, Park M, Imre A, Bedzyk MJ, No K, et al. Nanoscale piezoresponse studies of ferroelectric domains in epitaxial BiFeO₃ nanostructures. J Appl Phys 2009;105:061619–23.
- [12] Li X, Terabe K, Hatano H, Zeng H, Kitamura K. Domain patterning thin crystalline ferroelectric film with focused ion beam for nonlinear photonic integrated circuits. J Appl Phys 2006;100:106103–6.
- [13] Nagarajan V, Stanishevsky A, Ramesh R. Ferroelectric nanostructures via a modified focused ion beam technique. Nanotechnology 2006;17:338–43.
- [14] Li JY, Luo Y, Bai MJ, Ducharme S. Nanomesa and nanowell formation in Langmuir–Blodgett polyvinylidene fluoride trifluoroethylene copolymer films. Appl Phys Lett 2005;87:213116–8.
- [15] Bai MJ, Ducharme S. Ferroelectric nanomesa formation from polymer Langmuir–Blodgett films. Appl Phys Lett 2004;85:3528–30.
- [16] Hu ZJ, Tian MW, Nysten B, Jonas AM. Regular arrays of highly ordered ferroelectric polymer nanostructures for non-volatile low-voltage memories. Nat Mater 2009;8:62–7.
- [17] Yang H, Deschatelets P, Brittain ST, Whitesides GM. Fabrication of high performance ceramic microstructures from a polymeric precursor using soft lithography. Adv Mater 2001;13:54–8.
- [18] Seraji S, Wu Y, Jewell-Larson NE, Forbess MJ, Limmer SJ, Chou TP, et al. Patterned microstructure of sol-gel derived complex oxides using soft lithography. Adv Mater 2000;12:1421–4.
- [19] Chen S, Yao K, Tay FEH, Liow CL. Ferroelectric poly(vinylidene fluoride) thin films on Si substrate with the β phase promoted by hydrated magnesium nitrate. J Appl Phys 2007;102:104108–14.
- [20] Gregorio Jr R, Borges DS. Effect of crystallization rate on the formation of the polymorphs of solution cast poly(vinylidene fluoride). Polymer 2008;49: 4009–16.
- [21] Gregorio Jr R. Determination of the α, β, and γ crystalline phases of poly(vinylidene fluoride) films prepared at different conditions. J Appl Polymer Sci 2006;100:3272–9.
- [22] Vukicevic R, Beuermann S. Fullerenes decorated with poly(vinylidene fluoride). Macromolecules 2011;44:2597–603.
- [23] Benz M, Euler MB, Gregory OJ. The role of solution phase water on the deposition of thin films of poly(vinylidene fluoride). Macromolecules 2002;35:2682-8.
- [24] Park I, Ko SH, Pan H, Grigoropoulos CP, Pisano AP, Fréchet JMJ, et al. Nanoscale patterning and electronics on flexible substrate by direct nanoimprinting of metallic nanoparticles. Adv Mater 2008;20:489–96.
- [25] Park YJ, Kang YS, Park C. Micropatterning of semicrystalline poly(vinylidene fluoride) (PVDF) solutions. Eur Polym J 2005;41:1002–12.
- [26] Cauda V, Stassi S, Bejtka K, Canavese G. Nanoconfinement: an effective way to enhance PVDF piezoelectric properties. ACS Appl Mater Interfaces 2013;5(13): 6430-7.