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Electroactive behavior on demand in Poly(vinylidene fluoride-co-vinyl alcohol) copolymers

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ABSTRACT

Ferroelectric polymers, such as poly(vinylidene fluoride) (PVDF), are attractive electroactive materials that can be integrated in advanced electronic devices. Unfortunately, to obtain the ferroelectric phase in PVDF, additional processing methods or expensive copolymerizations with trifluoroethylene have to be employed. Moreover, the highly fluorinated polymers lack functionalities to gain improved properties, such as wettability and possibilities for crosslinking and nanoobject dispersion. In this work, the synthesis and electroactive behavior of poly(vinylidene fluoride-co-vinyl alcohol) (P(VDF-co-VA)) copolymers are demonstrated using a cheap vinyl acetate-based precursor. We show that the switching properties can be tuned by varying the vinyl alcohol content in the copolymers. Linear dielectric behavior is observed for copolymers with 10 mol % VA due to a mixture of α - and β -crystals. Intriguingly, the incorporation of 15 mol % VA results in the direct crystallization into the ferroelectric β -phase from the melt. Consequently, this P(VDF-co-VA) copolymer with hydroxyl functional groups in the polymer backbone is ferroelectric without additional processing and demonstrates a coercive field and a remnant polarization of 80 MV m⁻¹ and 2.8 μ C cm⁻² at 200 MV m⁻¹, respectively, showing its high potential for advanced electronic applications.

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1. Introduction

Ferroelectric polymers, including poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene (TrFE), are a class of materials showing a spontaneous electrical polarization that can be switched by the application of an electric field, while having excellent processability into light, tough and flexible films [1–3]. Therefore, bulk materials and thin films of PVDF based polymers find applications among others in memory storage devices, sensors, ferroelectric field-effect transistors and photovoltaics [4,5]. To obtain the desired electroactive properties, the highly fluorinated polymers have to crystallize in the ferroelectric β -phase, wherein the chains adopt an all-trans conformation [6]. Since PVDF crystallizes preferentially in the non-polar α -phase via melt

crystallization, numerous techniques to process PVDF in the β -phase are successfully investigated to control film thickness, crystal orientation and porosity [7,8]. An additional method to easily obtain the ferroelectric phase in PVDF is via copolymerizations with TrFE [9].

Regardless of the processing conditions, P(VDF-co-TrFE) copolymers, in the composition range of 50–80 mol% VDF, are always in the ferroelectric crystalline phase at room temperature [10]. Herein, the slightly bulkier TrFE units act as defects and increase the unit cell dimensions, which results in easier chain rotations around the polymer backbone leading to crystallization into the thermodynamically favorable all-trans conformation [11]. Even though P(VDF-co-TrFE) copolymers are already in industrial production, the hazardous storage and transport conditions of TrFE and the risk of explosions during synthesis make TrFE an expensive monomer, which rises the costs of the ferroelectric polymers [4]. Other approaches, like VDF copolymerization with chlorotrifluoroethylene (CTFE) followed by dechlorination, provide a safer

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alternative, yet strategies to get complete dechlorination with no dehydrofluorination have to be developed [12,13].

Copolymers of VDF with bulkier constituents, such as hexafluoropropylene (HFP) or monomers bearing functional groups (2-trifluoromethacrylic acid, allyl dimethyl phosphonate, etc.) usually yield smaller crystallites and the non-ferroelectric α -phase caused by the exclusion of the comonomers in the crystal lattice [14–16]. Even though reported in the literature, copolymers of VDF with non-fluorinated VAc attracted little attention, probably due to bulkiness and the high reactivity ratio between VDF and VAc and the possibility of chain transfer to monomer [17–19]. Nevertheless, controlling the amount of VAc and the subsequent hydrolysis of VAc units to vinyl alcohol (VA) provides an appealing method to

$$f_t = \frac{\int_{4.90}^{5.00} (\text{m}, -\text{CH}-, -\text{VAc} - \text{VAc} - \text{VAc}-)}{x}$$

$$f_d = \frac{\int_{5.18}^{5.38} (\text{m}, -\text{CH}-, -\text{VDF} - \text{VAc} - \text{VAc} - \text{VDF}-)}{x}$$

$$f_s = \frac{\int_{5.45}^{5.75} (\text{m}, -\text{CH}-, -\text{VDF} - \text{VAc} - \text{VDF}-)}{x}$$

$$\text{mol}\%_{\text{VAc}} = \frac{x}{x + \left(\frac{\int_{2.70}^{3.10} (\text{VDF}) + \int_{2.20}^{2.55} (\text{VDF and VAc}, -\text{CH}_2-) - 2f_s x - f_d x - \frac{2}{3}f_t x}{2} \right)}$$

include defects in the polymer backbone, while still having cocrystallization of VDF and VA due the small size of the VA monomer. Especially, since VAc is low-cost and easy in handling and storage, it provides major advantages over fluorinated monomers, such as TrFE and CTFE. Moreover, the introduction of alcohol moieties in the PVDF backbone gives opportunities to perform chemical modifications (e.g. isocyanate crosslinking), to induce better wetting to substrates and to strongly interact with nanoparticles.

2. Materials and methods

2.1. Materials

Vinyl acetate (Fluka, >99%) was dried over CaCl_2 and distilled under reduced pressure. Benzoyl peroxide (BPO) was recrystallized by adding methanol to a BPO solution in chloroform. Vinylidene fluoride (VDF, Synquest Labs, 98%), dimethyl carbonate (DMC, Acros, >99%, extra dry), hydrochloric acid (37%, Boom) were used as received. All other solvents were analytical grade.

2.2. Synthesis of P(VDF-co-VA) copolymers

The synthesis of P(VDF-co-VA) copolymers is shown in Scheme S1. Experimental details are outlined in the supporting information. ^1H -, ^{19}F -, and COSY NMR spectra were recorded on Varian (VXR) spectrometer operating at 400 MHz for the ^1H nucleus and 376 MHz for the ^{19}F nucleus. The molar content VAc was calculated according to the following equation:

$$x = \int_{4.90}^{5.00} (\text{m}, -\text{CH}-, -\text{VAc} - \text{VAc} - \text{VAc}-) + \int_{5.18}^{5.38} (\text{m}, -\text{CH}-, -\text{VDF} - \text{VAc} - \text{VAc} - \text{VDF}-) + \int_{5.45}^{5.75} (\text{m}, -\text{CH}-, -\text{VDF} - \text{VAc} - \text{VDF}-)$$

For the calculation of the molar content VAc, it is assumed that VAc sequences no longer than triads exist.

2.3. P(VDF-co-VA) copolymer film processing

A solution of the P(VDF-co-VA) copolymer in cyclopentanone (50 mg/mL) was cast on an aluminum Petri dish. The solvent was allowed to evaporate at 130 °C, from where the film was heated to the 160 °C. After removing the heating source and cooling down to ambient temperature, a free-standing film was obtained using a lift-off method in water.

2.4. Fourier transform infrared spectroscopy

The FTIR spectra of the copolymers were recorded on a Bruker Vertex 70 spectrophotometer using 32 scans at a nominal resolution of 4 cm^{-1} using a diamond single reflection attenuated total reflectance (ATR).

2.5. Wide-angle X-ray scattering

Wide-angle X-ray scattering (SAXS and WAXS) measurements was performed at beamline BM26B28 at the European Synchrotron Radiation Facility (ESRF) in Grenoble with a wavelength $\lambda = 0.97\text{ \AA}$. The WAXS pattern was acquired over a time interval of 30 s using a Pilatus 300 K detector (1472×195 pixels of $172\text{ }\mu\text{m} \times 172\text{ }\mu\text{m}$) placed at a distance of 0.28 m. The scattering vector q is defined as

$q = 4\pi/\lambda(\sin \theta)$ with 2θ being the scattering angle. Deconvolution of the WAXS profiles was achieved using MATLAB. The experimental profiles were deconvoluted by using the sum of a linear background and pseudo-Voigt peaks describing the scattering from the amorphous and the crystalline phases.

2.6. Thermal characterization

DSC thermograms were recorded on a TA Instruments DSC Q1000. TGA thermograms were recorded on a Parkin Elmer Thermogravimetric Analyzer TGA7 under a N_2 atmosphere. The heating and cooling rate was set to be $10\text{ }^\circ\text{C min}^{-1}$.

2.7. Electrical characterization

D-E and I-E loops were obtained using a state-of-the-art aixACCT TF2000E ferroelectric tester where AC electric fields (up to 10 kV) were applied across the polymer films with a triangular waveform at a frequency of 10 Hz. Chromium (5 nm)/gold (100 nm) electrodes with a diameter of 2 mm were deposited on both sides of P(VDF-co-VA) copolymer films by vapor deposition. Chromium was used only as adhesion layer. Silicon oil was used to prevent flashovers.

3. Results and discussion

In this work, we show the copolymerizations of VDF with VAc followed by the hydrolysis to P(VDF-co-VA) copolymers and demonstrate its electroactive behavior. The copolymers described in this work are designated according to the copolymer composition ratio determined by ^1H NMR spectroscopy. As proof of concept, solution copolymerizations of VDF and VAc are performed in dimethyl carbonate (DMC) using benzoyl peroxide as initiator (Scheme S1). Asandai and co-workers compared a large range of solvents for photopolymerizations of VDF and they found that DMC shows is the best trade-off between chain transfer and having fast reaction rates [20]. Since there is a strong tendency for the propagation of VAc, the amount of VAc added to polymerization mixture is low and the reaction time is kept short to avoid compositional drift [18,19]. After the polymerization, the presence of unreacted VAc was confirmed using ^1H NMR spectroscopy, indicating the absence of PVDF homopolymers. Subsequently, the P(VDF-co-VAc) copolymers were hydrolyzed in a dioxane/hydrochloric acid mixture to yield P(VDF-co-VA) copolymers. Even though, base hydrolysis is commonly used to hydrolyze PVAc, acidic conditions prevent dehydrofluorination processes, while preserving the white color of the final product. Even though cheap resources are used to synthesize P(VDF-co-VA) copolymers, future work should be devoted in optimizing the reactor conditions, such as using a flow process or batch polymerization with a constant inlet of VAc, to increase VDF conversion.

Unravelling the complete microstructure of PVDF-based copolymers is a challenging task due to the large number of possible monomer sequences caused by the monomer distribution, monomer inversions, initiator fragments and backbiting reactions [21–23]. Therefore, we primarily focus on proving the inclusion of VAc (and consequently VA) units in the polymer backbone.

In Fig. 1, the ^1H NMR spectrum of P(VDF₈₅-co-VAc₁₅) shows the characteristic VDF signals (head-to-tail addition) located in between 2.70 and 3.10 ppm, whereas the protons corresponding to the tail-to-tail additions are at 2.20–2.55 ppm overlapping with the signals from the methylene protons from VAc. The methyl peak appears at 2.00 ppm, which is similar to PVAc homopolymers since no significant changes in the local environment of the protons are experienced. On contrary, the methine group of VAc is separated in three isolated signals at 4.90–5.00 ppm,

Fig. 1. ^1H NMR spectra of P(VDF₈₅-co-VAc₁₅) and P(VDF₈₅-co-VA₁₅) showing the successful hydrolysis.

5.18–5.38 ppm and 5.45–5.75 ppm, showing different linkages in the P(VDF-co-VAc) polymer backbone. The weak signal at 4.90–5.00 ppm corresponds to methine protons included in at least triads of VAc-VAc-VAc sequences just as for PVAc homopolymers. Interestingly, the amount of dyads (5.18–5.38 ppm) or isolated VAc units (5.45–5.75 ppm) is much higher, indicating the randomness of the copolymerization [17]. The amount of VAc in the copolymer was determined to be 15 mol% by integrating the methine protons and compare them the VDF protons in the backbone (Eq. S1). ^1H NMR correlation spectroscopy (COSY) (Fig. S4) was used to correlate the backbone methylene protons to the methine protons of VAc. Having in mind the symmetrical nature around the methine proton at 5.45–5.75 ppm, indeed, a single cross peak with the VDF methylene protons (2.41 ppm) is observed, proving the isolation of methine protons in the VDF-VAc-VDF sequence. As expected, the methine protons in the -VDF-VAc-VAc-VDF- dyads show two cross peaks in the ^1H NMR COSY. Similar to the isolated VAc units, one correlation (5.30–2.35 ppm) connects the methylene of VAc next the $-\text{CF}_2-$ unit to the methine protons, whereas the other cross peak (5.30–1.98 ppm) is correlating the methine proton to the methylene of the sequential VAc entity. Since the methine proton signals located in between 4.90 and 5.00 ppm are sandwiched between VAc units only one correlation (4.94–1.90 ppm) appears.

After acidic treatment of P(VDF₈₅-co-VAc₁₅), the complete up-field shift of the methine protons to 3.90–4.50 ppm and the disappearance of the methyl peak indicate the complete hydrolysis to P(VDF₈₅-co-VA₁₅) as shown in Fig. 1. As already observed for the P(VDF₈₅-co-VAc₁₅) copolymer, the signals corresponding to the different sequences of VA can be distinguished using ^1H NMR COSY. A strong cross peak is observed for the isolated VA units at 4.34–2.26 ppm correlating with the methylene next to the $-\text{CF}_2-$ unit. As abovementioned, the dyads show two cross peaks of methine protons at 4.22–2.18 ppm and 4.22–1.66 ppm, showing the interactions with the methylene next to the $-\text{CF}_2-$ unit and with the methylene of the sequential VAc entity, respectively.

In addition to the P(VDF₈₅-co-VA₁₅) copolymer, a P(VDF₉₀-co-VAc₁₀) copolymer with 10 mol% of VAc is prepared and subsequently hydrolyzed to P(VDF₉₀-co-VA₁₀). Interestingly, the lower content of VAc in the copolymerization results in the absence of VAc triads in the polymer backbone as demonstrated in the ^1H NMR (COSY) spectra (Figs. S1 and S2).

P(VDF-co-VA) copolymer films were cast from cyclopentanone at 130 °C, which is above the crystallization temperature of the polymers. Subsequently, the films were heated to 160 °C followed by quenching to ambient temperature to ensure complete removal of solvent and to obtain the crystalline structure from the melt. Finally, free standing films are obtained using a lift-off method in water.

To ensure that no degradation processes occur in the application range of the ferroelectric materials, good thermal stability of the P(VDF-co-VA) copolymers is confirmed with thermal gravimetric analysis (Fig. S14). The differential scanning calorimetry (DSC) profiles of the P(VDF-co-VA) copolymers are depicted in Fig. 2b. As expected, due to the introduction of comonomers in PVDF backbone the crystallization and melting temperatures (T_c and T_m) are significantly reduced to $T_c = 93$ °C and $T_m = 125$ °C for P(VDF₈₅-co-VA₁₅) and $T_c = 105$ °C and $T_m = 135$ °C for P(VDF₉₀-co-VA₁₀), whereas PVDF homopolymers show crystallization and melting temperatures that are at least 30 °C higher [1]. Interestingly, the crystallization and melting temperature is lower than for P(VDF-co-TrFE) copolymers with comparable compositions and no Curie transition is observed in contrast to the copolymers with TrFE. Noteworthy, the bulky VAc units impede crystallization of the P(VDF₈₅-co-VAc₁₅) copolymer and consequently a completely amorphous copolymer is obtained, whereas P(VDF₉₀-co-VAc₁₀) still crystallizes albeit at a lower temperature. Similar observations are made for P(VDF-co-HFP) copolymers, wherein a molar content of >19 mol% HFP prevents crystallization yielding a fully amorphous elastomer [14].

Fourier transform infrared (FTIR) spectroscopy and Wide-angle X-ray scattering (WAXS) are used to identify the crystalline phases in the P(VDF-co-VA) copolymers after melt crystallization. In Fig. 2a, the FTIR spectrum of the P(VDF₈₅-co-VA₁₅) copolymer demonstrates the all-trans conformation of the polymer chains due

to the absorption bands located at 510, 840, 1273 cm^{-1} , indicating β -phase formation [6]. In addition, no characteristic absorption bands corresponding to the crystalline α -phase or γ -phase are observed, proving that P(VDF₈₅-co-VA₁₅) crystallized solely in the β -phase. Furthermore, the WAXS profile (Fig. 2d) shows one peak at $q = 14.55 \text{ nm}^{-1}$ ($d = 4.32 \text{ \AA}$) identifying the (110/200) crystal planes, which belong to the ferroelectric crystalline phase. On the contrary, the FTIR spectrum of P(VDF₉₀-co-VA₁₀) shows, next to the β -phase absorption bands, characteristic signals corresponding to the α -phase located at 612, 760 and 796 cm^{-1} . In addition, the WAXS profile depicted in Fig. 2c, confirms the coexistence of the α - and β -phase in the P(VDF₉₀-co-VA₁₀) copolymer due to appearance of the (100), (020) and (110) reflections at 12.70, 13.20 and 14.25 nm^{-1} , respectively, besides the scattering corresponding to the (110/200) crystal planes of the β -phase appearing as shoulder to the (110) α -phase reflections. The difference in crystalline phases for the copolymers is ascribed to the molar content of vinyl alcohol. The lack of defects in P(VDF₉₀-co-VA₁₀) results in crystallization into the α -phase, like pure PVDF, whereas vinyl alcohol rich parts still crystallize in the β -phase. The coexistence of the α - and β -phase in P(VDF₉₀-co-VA₁₀) is also clearly visible in the deconvoluted WAXS profiles. The overall volumetric crystallinity is determined to be 55% from which 82% are α -phase crystals and 18% is in the β -phase. P(VDF₈₅-co-VA₁₅) crystallizes in the β -phase with a degree of crystallinity of 38%. Melt crystallization of P(VDF-co-VA) copolymers directly into the β -phase is unique for PVDF-based copolymers. PVDF usually crystallizes in the kinetically favorable α -phase, whereas P(VDF-co-TrFE) copolymers first crystallize into the paraelectric phase before undergoing a crystalline phase transition to the ferroelectric phase at lower temperatures. In literature, to overcome crystallization into the α -phase, ultrafast cooling and confined crystallization effectively reduce the crystallization temperature of PVDF [24,25]. Another approach to

Fig. 2. a) FTIR spectra, b) DSC thermograms and WAXS profiles for c) P(VDF₉₀-co-VA₁₀) and d) P(VDF₈₅-co-VA₁₅).

induce β -phase formation is *via* the addition of charged nanofillers or ionic liquids [6,26,27]. In here, the negatively charged surfaces from the nanoparticles or ionic liquid counterions interact with positively charged CH_2 units in the PVDF backbone, inducing an all-trans conformation [6,28]. Unfortunately, a drawback of these methods is that external processing equipment or additional materials have to be used in order to obtain the β -phase. In our case, the introduction of defects and the slightly increased interplanar distances of the P(VDF-co-VA) copolymer compared to PVDF in the β -phase drives the formation of the ferroelectric crystalline phase directly from the melt, while having functionalities to further enhance or tune the materials properties.

The electroactive behavior of the P(VDF-co-VA) copolymer films was investigated by applying an electric field up to 200 MV m^{-1} in a triangular wave form at a frequency of 10 Hz, measuring the polarization as the integral of the resulting current. Indeed, a typical hysteresis loop, demonstrated in Fig. 3, confirms the ferroelectric behavior of the P(VDF₈₅-co-VA₁₅) copolymer, wherein the coercive field is found to be 80 MV m^{-1} and the remnant polarization is $2.8 \text{ } \mu\text{C cm}^{-2}$. Probably, since the interplanar distance of the P(VDF-co-VA) copolymer is in between the interplanar distance of PVDF and P(VDF-co-TrFE), the coercive field is in between that of PVDF and P(VDF-co-TrFE), whereas the lower degree of crystallinity and physical pinning of VA units (due to the lower dipole moment compared to VDF and TrFE) in the crystalline structure enhances dipole reversibility resulting in a lower remnant polarization [29,30]. In contrast, as demonstrated in Fig. 3, the P(VDF₉₀-co-VA₁₀) copolymer shows linear dielectric behavior, even though the coexistence of the α - and β -phase in the films. The linear increase of polarization as function of electric field is a result of the zero net dipole moment α -phase plus the isolation and small number of β -crystals resulting in a much lower polarization at similar electric fields than the ferroelectric P(VDF₈₅-co-VA₁₅) copolymer.

Additionally, the charge-discharge efficiency is calculated from the unipolar polarization-electric field loops as demonstrated in Fig. 3c. As expected, ferroelectric P(VDF₈₅-co-VA₁₅) shows much lower efficiencies (47% vs 72%, respectively) above the coercive field than linear dielectric P(VDF₉₀-co-VA₁₀) due to the high remnant polarization. Nevertheless, similar discharge energy densities are obtained due to the non-linear behavior of ferroelectric materials resulting in a high polarization. Interestingly, the high efficiencies for P(VDF₉₀-co-VA₁₀) shows its potential to be used in capacitive energy storages applications. At 300 MV m^{-1} , the discharged energy density is determined to 5.4 J cm^{-3} for P(VDF₉₀-co-VA₁₀), whereas the golden standard, biaxially oriented polypropylene, displays a discharged energy density of 1.3 J cm^{-3} at the same field [31].

4. Conclusions

We demonstrate the electroactive behavior of P(VDF-co-VA) copolymers. Using VAc as a cheap comonomer and an easy free radical polymerization in solution, P(VDF-co-VAc) copolymers are successfully synthesized and subsequently hydrolyzed to P(VDF-co-VA). When 15 mol % VA is included in the copolymer, melt crystallization directly into the β -phase results in ferroelectric behavior, excluding the requirement of the extra processing methods. The coercive field and remnant polarization are determined to be 80 MV m^{-1} and $2.8 \text{ } \mu\text{C cm}^{-2}$ at 200 MV m^{-1} , respectively. On contrary, the inclusion of 10 mol % VA leads to a mixture the α - and a small amount of β -crystals resulting in linear dielectric behavior with high charge-discharge efficiencies and a discharged energy density of 5.4 J cm^{-3} at 300 MV m^{-1} , showing the versatility in electroactive behavior of P(VDF-co-VA) copolymers by simply changing the VA content. We envision that P(VDF-co-VA) copolymers, due to the introduction of hydroxyl groups in the polymer backbone, provides a platform for advanced materials with tunable electroactive properties in bulk and thin film applications.

Fig. 3. Bipolar Polarization/Current-Electric Field loops for a) P(VDF₉₀-co-VA₁₀) and b) P(VDF₈₅-co-VA₁₅). c) Discharge energy densities and charge-discharge efficiencies for the P(VDF₉₀-co-VA₁₀) and P(VDF₈₅-co-VA₁₅) copolymers obtained from unipolar loops. All measurements were obtained at room temperature using a triangular wave form at 10 Hz.

Declarations of interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mtener.2018.10.019>.

References

- [1] B. Ameduri, From Vinylidene Fluoride (VDF) to the applications of VDF-containing polymers and copolymers: recent developments and future trends, *Chem. Rev.* 109 (2009) 6632–6686, <https://doi.org/10.1021/cr800187m>.
- [2] A.J. Lovinger, Ferroelectric polymers, *Science* 220 (1983) 1115–1121, <https://doi.org/10.1126/science.220.4602.1115>.
- [3] V.S.D. Voet, G. ten Brinke, K. Loos, Well-defined copolymers based on poly(vinylidene fluoride): from preparation and phase separation to application, *J. Polym. Sci. Polym. Chem.* 52 (2014) 2861–2877, <https://doi.org/10.1002/pola.27340>.
- [4] T. Soulestin, V. Ladmiral, F.D. Dos Santos, B. Ameduri, Vinylidene fluoride- and trifluoroethylene-containing fluorinated electroactive copolymers. How does chemistry impact properties? *Prog. Polym. Sci.* 72 (2017) 16–60, <https://doi.org/10.1016/j.progpolymsci.2017.04.004>.
- [5] X. Chen, X. Han, Q.-D. Shen, PVDF-based ferroelectric polymers in modern flexible electronics, *Advanced Electronic Materials* 3 (2017), 1600460, <https://doi.org/10.1002/aelm.201600460>.
- [6] P. Martins, A.C. Lopes, S. Lancers-Mendez, Electroactive phases of poly(vinylidene fluoride): determination, processing and applications, *Prog. Polym. Sci.* 39 (2014) 683–706, <https://doi.org/10.1016/j.progpolymsci.2013.07.006>.
- [7] C. Ribeiro, C.M. Costa, D.M. Correia, J. Nunes-Pereira, J. Oliveira, P. Martins, R. Gonçalves, V.F. Cardoso, S. Lancers-Méndez, Electroactive poly(vinylidene fluoride)-based structures for advanced applications, *Nat. Protoc.* 13 (2018) 681–704, <https://doi.org/10.1038/nprot.2017.157>.
- [8] V. Sencadas, R.G. Jr, S. Lancers-Méndez, α to β phase transformation and microstructural changes of PVDF films induced by uniaxial stretch, *J. Macromol. Sci. Part B.* 48 (2009) 514–525, <https://doi.org/10.1080/00222340902837527>.
- [9] T. Furukawa, M. Date, E. Fukada, Y. Tajitsu, A. Chiba, Ferroelectric behavior in the copolymer of vinylidene fluoride and trifluoroethylene, *Jpn. J. Appl. Phys.* 19 (1980), L109, <https://doi.org/10.1143/JJAP.19.L109>.
- [10] T. Yagi, M. Tatemoto, J. Sako, Transition behavior and dielectric properties in trifluoroethylene and vinylidene fluoride copolymers, *Polym. J.* 12 (1980) 209–223, <https://doi.org/10.1295/polymj.12.209>.
- [11] T. Furukawa, Structure and functional properties of ferroelectric polymers, *Adv. Colloid Interface Sci.* 71–72 (1997) 183–208, [https://doi.org/10.1016/S0001-8686\(97\)90017-8](https://doi.org/10.1016/S0001-8686(97)90017-8).
- [12] S. Tan, J. Li, G. Gao, H. Li, Z. Zhang, Synthesis of fluoropolymer containing tunable unsaturation by a controlled dehydrochlorination of P(VDF-co-CTFE) and its curing for high performance rubber applications, *J. Mater. Chem.* 22 (2012) 18496–18504, <https://doi.org/10.1039/C2JM33133K>.
- [13] Y. Lu, J. Claude, B. Neese, Q. Zhang, Q. Wang, A modular approach to ferroelectric polymers with chemically tunable Curie temperatures and dielectric constants, *J. Am. Chem. Soc.* 128 (2006) 8120–8121, <https://doi.org/10.1021/ja062306x>.
- [14] T.S. Ahmed, J.M. DeSimone, G.W. Roberts, Continuous copolymerization of vinylidene fluoride with hexafluoropropylene in supercritical carbon Dioxide: low hexafluoropropylene content semicrystalline copolymers, *Macromolecules* 40 (2007) 9322–9331, <https://doi.org/10.1021/ma0713613>.
- [15] S. Banerjee, M. Wehbi, A. Manseri, A. Mehdi, A. Alaaeddine, A. Hachem, B. Ameduri, Poly(vinylidene fluoride) containing phosphonic acid as anticorrosion coating for steel, *ACS Appl. Mater. Interfaces* 9 (2017) 6433–6443, <https://doi.org/10.1021/acsami.6b15408>.
- [16] M. Wehbi, S. Banerjee, A. Mehdi, A. Alaaeddine, A. Hachem, B. Ameduri, Vinylidene fluoride-based polymer network via cross-linking of pendant triethoxysilane functionality for potential applications in coatings, *Macromolecules* 50 (2017) 9329–9339, <https://doi.org/10.1021/acs.macromol.7b02138>.
- [17] V. Panchalingam, J.R. Reynolds, New vinylidene fluoride copolymers: poly(vinyl acetate-co-vinylidene fluoride), *J. Polym. Sci. C Polym. Lett.* 27 (1989) 201–208, <https://doi.org/10.1002/pol.1989.140270605>.
- [18] J. Brandrup, E.H. Immergut, E.A. Grulke, *Polymer Handbook*, fourth ed., Wiley, 2004.
- [19] B. Baradie, M.S. Shoichet, Synthesis of fluorocarbon–vinyl acetate copolymers in supercritical carbon dioxide: insight into bulk properties, *Macromolecules* 35 (2002) 3569–3575, <https://doi.org/10.1021/ma010461k>.
- [20] A.D. Asandei, O.I. Adebolu, C.P. Simpson, Mild-temperature Mn2(CO)10-photomediated controlled radical polymerization of vinylidene fluoride and synthesis of well-defined poly(vinylidene fluoride) block copolymers, *J. Am. Chem. Soc.* 134 (2012) 6080–6083, <https://doi.org/10.1021/ja300178r>.
- [21] E.B. Twum, C. Gao, X. Li, E.F. McCord, P.A. Fox, D.F. Lyons, P.L. Rinaldi, Characterization of the chain-ends and branching structures in poly(vinylidene fluoride) with multidimensional NMR, *Macromolecules* 45 (2012) 5501–5512, <https://doi.org/10.1021/ma300835s>.
- [22] M. Guerre, B. Campagne, O. Gimello, K. Parra, B. Ameduri, V. Ladmiral, Deeper insight into the MADIX polymerization of vinylidene fluoride, *Macromolecules* 48 (2015) 7810–7822, <https://doi.org/10.1021/acs.macromol.5b01528>.
- [23] M. Pianca, E. Barchiesi, G. Esposto, S. Radice, End groups in fluoropolymers, *J. Fluorine Chem.* 95 (1999) 71–84, [https://doi.org/10.1016/S0022-1139\(98\)00304-2](https://doi.org/10.1016/S0022-1139(98)00304-2).
- [24] M. Pan, L. Yang, J. Wang, S. Tang, G. Zhong, R. Su, M.K. Sen, M.K. Endoh, T. Koga, L. Zhu, Composite poly(vinylidene fluoride)/polystyrene latex particles for confined crystallization in 180 nm nanospheres via emulsifier-free batch seeded emulsion polymerization, *Macromolecules* 47 (2014) 2632–2644, <https://doi.org/10.1021/ma500249p>.
- [25] N.L. Meereboer, I. Terzić, S. Saidi, D. Hermida Merino, K. Loos, Nanoconfinement-induced β -phase formation inside poly(vinylidene fluoride)-based block copolymers, *ACS Macro Lett.* (2018) 863–867, <https://doi.org/10.1021/acsmacrolett.8b00418>.
- [26] A.C. Lopes, C. Ribeiro, V. Sencadas, G. Botelho, S. Lancers-Méndez, Effect of filler content on morphology and physical–chemical characteristics of poly(vinylidene fluoride)/NaY zeolite-filled membranes, *J. Mater. Sci.* 49 (2014) 3361–3370, <https://doi.org/10.1007/s10853-014-8043-4>.
- [27] R. Mejri, J.C. Dias, A.C. Lopes, S. Bebes Hentati, M.M. Silva, G. Botelho, A. Mão de Ferro, J.M.S.S. Esperança, A. Maceiras, J.M. Laza, J.L. Vilas, L.M. León, S. Lancers-Méndez, Effect of ionic liquid anion and cation on the physico-chemical properties of poly(vinylidene fluoride)/ionic liquid blends, *Eur. Polym. J.* 71 (2015) 304–313, <https://doi.org/10.1016/j.eurpolymj.2015.07.058>.
- [28] Y. Wu, S.L. Hsu, C. Honeker, D.J. Bravet, D.S. Williams, The role of surface charge of nucleation agents on the crystallization behavior of poly(vinylidene fluoride), *J. Phys. Chem. B* 116 (2012) 7379–7388, <https://doi.org/10.1021/jp3043494>.
- [29] N. Tsutsumi, R. Kosugi, K. Kinashi, W. Sakai, Nature of the enhancement in ferroelectric properties by gold nanoparticles in vinylidene fluoride and trifluoroethylene copolymer, *ACS Appl. Mater. Interfaces* 8 (2016) 16816–16822, <https://doi.org/10.1021/acsami.6b05897>.
- [30] L. Zhu, Exploring strategies for high dielectric constant and low loss polymer dielectrics, *J. Phys. Chem. Lett.* 5 (2014) 3677–3687, <https://doi.org/10.1021/jz501831q>.
- [31] Y. Zhao, Q. Li, X. Zhang, H. Li, J. Lu, Z. Zhang, High energy density and discharging efficiency achieved in chlorinated polyethylene films for high energy-storage applications, *Macromol. Chem. Phys.* 219 (2018), 1700621, <https://doi.org/10.1002/macp.201700621>.