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Structure and ferroelectric properties of P(VDF-TrFE) films prepared under different conditions — Effect of filtration of the copolymer solution

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Vinylidene fluoride-trifluoroethylene copolymer films of molar ratio 70/30 with thickness of about 1 μm have been deposited from solution in ethyl methyl ketone to a glass substrate with an aluminum electrode by spin coating. The solution has been filtrated through a PTFE membrane filter with pore size 0.2 μm directly before spin coating or it has been used as is (unfiltrated). After deposition of a top electrode, the samples have been polarized by hysteresis loops with an electric field amplitude of about 100 V/μm. In samples, annealed at temperature 145°C for 3 h, a high remanent polarization of about 7.5 μC/cm^2 has been achieved, without significant differences between samples fabricated of filtrated or unfiltrated solution. Spherulitic lamella are growing in films fabricated of filtrated solution when they are heated above the melting temperature to 159°C for 3 min before the further annealing process at 145°C. These films show substantially lower remanent polarization below 4 μC/cm^2. Pyroelectric images recorded with a pyroelectric laser scanning microscope show that the spherulites have very small pyroelectric activity, i.e., the spherulites consist of flat-on lamella. In contrast, no spherulitic lamella are growing in films fabricated of unfiltrated solution heated above the melting temperature, melted and annealed under the same conditions. An explanation for this observation is that filtrating changes the structure of the copolymer in solution from polymer coil to rod. Copolymer rods deposited on a substrate will crystallize in flat-on lamella when heated above the melting temperature, in contrast to copolymer coils which crystallize in edge-on lamella.

Keywords: P(VDF-TrFE); ferroelectric; polymer; structure.

1. Introduction

The copolymer of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) is semicrystalline consisting of crystalline and noncrystalline regions. As ferroelectricity originates from the crystalline phase the degree of crystallinity is an essential factor for the performance of the material. To increase grain size and crystallinity, annealing processes are commonly applied to VDF-TrFE copolymer film deposited from solution. It is common to anneal the material at temperatures above the Curie temperature but below the melting temparature of the material.[1] Details in the annealing process are of high importance. Variations of the annealing temperature of 1 K only can have significant effect on the morphology and structure of VDF-TrFE copolymer films.

It is usually avoided to melt a film deposited from solution as the intensity of (110) + (200) diffraction peaks attributed to the β phase of P(VDF-TrFE) decreases.[2,3] Even irreversible extinction of ferroelectric polarization in spin-coated VDF-TrFE copolymer thin films upon melting and recrystallization has been observed.[4] It has been reported that the β-phase content shows its maximum at 140°C annealing temperature.[5] Morphologic transition from big grains to fiber-like rods has been observed for VDF-TrFE copolymer film of molar ratio 70/30 above the melting temperature.[6] However, not only decrease but also increase of the ferroelectric diffraction peak is reported in literature. For a spray-coated VDF-TrFE copolymer film it has been found that neither peak intensity nor degree of crystallinity decreases for annealing at 170°C.[7] It is also reported that annealing above the melting temperature results in an increase of the ferroelectric peak and the disappearance of peaks resulting from the nonpolar phase.[8]

Dust particles and other impurities in the polymer solution can generate defects in the deposited copolymer film which may e.g., cause a breakdown when the film is polarized under high electric field. A common procedure to remove such particles and increase the yield of high quality films is to filtrate the copolymer solution before deposition on a substrate. In our laboratory filtrated solution is sometimes used for the fabrication of copolymer film, but not always. Characterizing VDF-TrFE copolymer film prepared from unfiltrated and filtrated solution has led to the initially unexpected observation that filtering can have a significant effect on structure and ferroelectric properties. This was the motivation for a more detailed study presented in the following.

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2. Experimental

VDF-TrFE copolymer of molar ratio 70/30 from Solvay has been dissolved in methyl ethyl ketone (MEK) in a mass concentration of 10%. The solution has been dropped on a glass substrate, which was covered with an aluminum electrode line of 1 mm width. The solution has been either filtrated through a PTFE membrane filter with 0.2 μm pore size directly before spin coating or it has been used as is (unfiltrated). Films of about 1.2 μm thickness have been fabricated by spin coating with rotational speed 1400 revolutions per minute. A 1 mm wide aluminum line has been evaporated to the top surface of the film, oriented orthogonal to the aluminum line on the substrate, forming a sample electrode of 1 mm by 1 mm.

Samples D76u (unfiltrated) and D76f (filtrated) have been annealed at temperature 120°C for 2 h. Samples D87u and D87f have been annealed at 145°C for 3 h and then cooled down 120°C within 2 h. Samples D62u and D62f have been heated to 159°C which is above the melting temperature, kept at this temperature for 3 min, and cooled to 145 °C within 15 min. Subsequently, they have then been further annealed at this temperature for 3 h and then cooled down 120°C within 2 h.

Optical images of the samples have been taken with a microscope Stemi 2000-C with camera AxioCam ICc 3 from Zeiss.

The crystalline structure has been characterized by X-ray diffraction (XRD) using a D8 Discover of Bruker AXS with wavelength $\lambda = 1.5406$ Å (Cu-K_α) in reflective Θ–2Θ mode.

Hysteresis loops have been measured using a modified Sawyer-Tower circuit at a frequency of 10 Hz. Starting at about 40 V/μm the electric field amplitude has been increased in steps up to 105 V/μm. At each value of the electric field amplitude about 600 loops have been recorded, allowing the remanent polarization to be stabilized.

Two-dimensional images of the pyroelectric activity have been recorded with a laser-scanning microscope.[9,10] The beam of a laser diode with wavelength $\lambda = 405$ nm has been focused onto a spot with diameter smaller than 1 μm on the top electrode. Modulating the laser intensity generates a pyroelectric ac signal in the heated spot. The resulting pyroelectric current has been amplified by a current-to-voltage converter type DHPCA-100 from FEMTO Messtechnik GmbH and measured with a lock-in amplifier type HF2LI from Zurich Instruments. Two-dimensional images of the pyroelectric activity have been recorded by scanning the surface of the sample line by line with the laser spot.

3. Results and Discussion

Microscopic images of the samples are shown in Fig. 1. No structures are visible in samples D76u and D76f which had been heated to a maximum temperature of 120°C during the annealing process. Slightly expressed structures are visible in samples D87u and D87f from unfiltrated and filtrated solutions which had been heated up to 145°C. The structures seen in the samples D62u and D62f heated to 159°C (above the melting temperature) are very different. Sample D62u shows only slightly expressed structures like the samples annealed at 145°C. In contrast, sample D62f prepared from filtrated solution shows very large plate-like structures. Figure 2 shows the AFM image of sample D62f recorded with an atomic force microscope type Keysight 5600LS SPM at a place not covered by the top electrodes. A spherulitic structure larger than the scan area of 70 μm × 70 μm is seen. For comparison the AFM image of sample D70f is also shown. Sample D70f has been treated with the same temperature profile as sample D62f, only the annealing time duration at

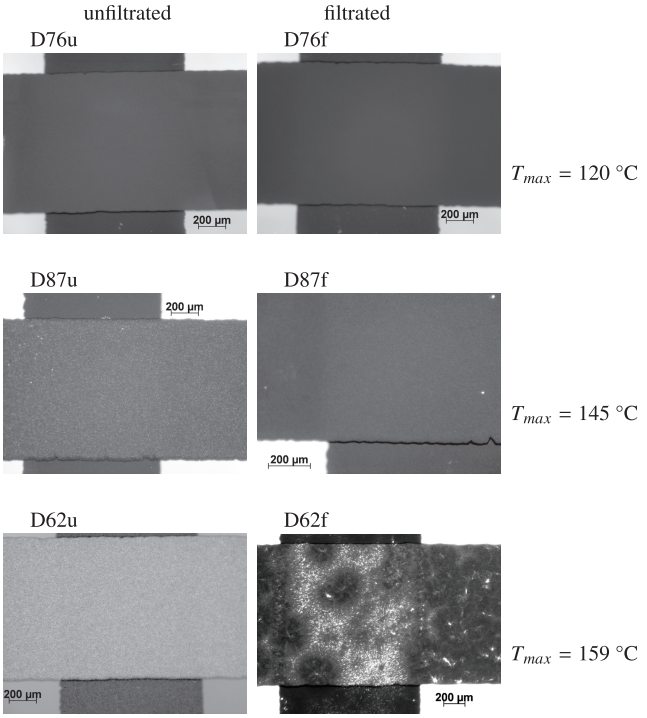

Fig. 1. Microscopic images of samples D76u, D76f, D87u, D87f, D62u and D62f. The samples in the left and right columns are prepared from unfiltrated and filtrated solution, respectively. The maximum temperatures of the thermal annealing process are indicated at the right side.

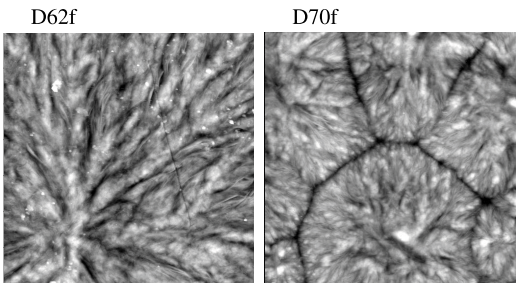

Fig. 2. AFM images of samples D62f and D70f. The scan area is 70 μm × 70 μm.

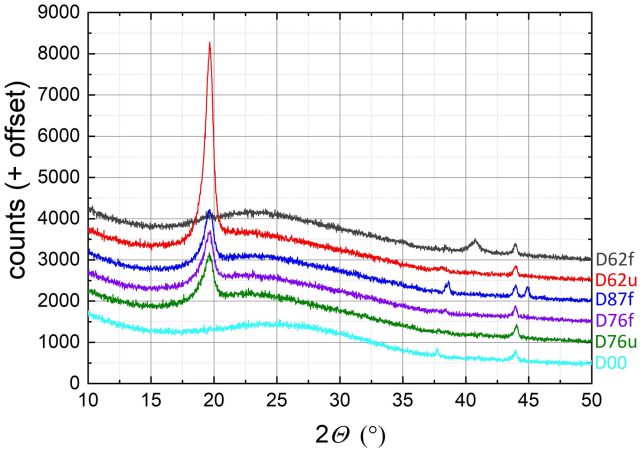

Fig. 3. X-ray diffraction curves of glass substrate D00 and samples D76u, D76f, D87f, D62u, D62f, measured at room temperature with wavelength $\lambda = 1.5406$ Å (Cu-K_α) in reflective Θ–2Θ mode. For better visability offsets of 500, 1000, 1500, 2000 and 2500 counts have been added to the curves of samples D76u, D76f, D87f, D62u and D62f, respectively.

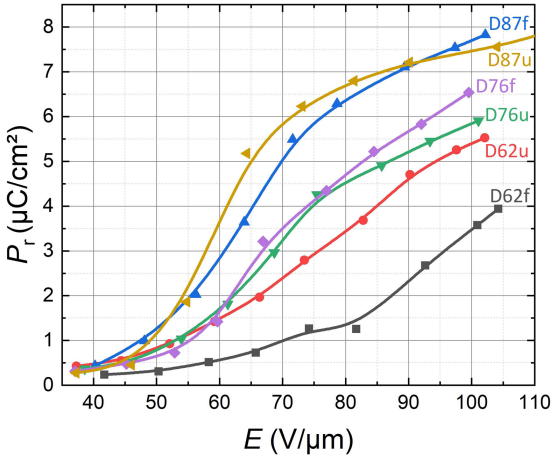

Fig. 4. Remanent polarization P_r of the samples recorded with hysteresis loops as a function of the electric fieled amplitude E.

145°C was shortened to 1 h instead of 3 h. As a consequence smaller spherulites have grown. The spherulitic structures visible in the AFM images indicate the spherulitic nature of the platelike structures of sample D62f in Fig. 1.

Figure 3 shows the X-ray diffraction curves of samples D76u, D76f, D87f, D62u, D62f and of a glass substrate (D00), measured at room temperature with wavelength $\lambda = 1.5406$ Å (Cu-K_α) in reflective Θ–2Θ mode. The samples from filtrated and unfiltrated solution, annealed at 120°C and at 145°C are showing essentially the same diffraction curves with respect to peak positions as well as to peak amplitudes (counts). Most prominent is the (200) + (110) Bragg reflection at 2Θ = 19.8°.[11,12] Substantially different are the diffraction curves of the samples which had been molten at 159°C. The (200) + (110) Bragg reflection of the sample fabricated from the filtrated solution is essentially disappeared, and the (201) + (111) Bragg reflection at 2Θ = 40.85°[11] arises. In contrast, the (200) + (110) Bragg reflection of the sample fabricated from unfiltrated solution is very strong with an intensity four times higher than of the unmolten samples. This indicates that the VDF-TrFE copolymer film which solidifies from the melt crystallizes in flat-on lamella when the film was fabricated from filtrated solution, but in edge-on lamella for film fabricated from filtrated solution. The very high intensity of the (200) + (110) Bragg reflection of the sample fabricated from unfiltrated solution and molten can not be caused by an accordingly higher crystallinity. A possible explanation is that the crystallites are significantly better aligned in parallel to the substrate surface than in samples which had not been molten.

The remanent polarization of the samples as a function of the applied electric field amplitude is shown in Fig. 4. At amplitude $E = 100$ V/μm the samples annealed at 120°C show $P_r = 5.8$ μC/cm² and $P_r = 6.5$ μC/cm². The sample fabricated from filtrated solution shows a slightly higher P_r than the one fabricated from unfiltrated solution. The samples annealed at 145°C show $P_r = 7.5$ μC/cm² and $P_r = 7.8$ μC/cm². Again the sample fabricated from filtrated solution shows a slightly higher P_r than the one fabricated from unfiltrated solution, but also a higher coercive field.

The pyroelectric image of sample D62f is shown in Fig. 5. The modulation frequency of the laser intensity was $f = 134$ kHz. Wich a thermal diffusivity $D = 1.12\ 10^{-7}$ m²/s this corresponds to the pyroelectric activity in a distance $d = 515$ nm below the heated top electrode, i.e. nearly in the middle of the copolymer film.[13,14] The same spherulitic structures which are seen in the microscopic image in Fig. 1 are visible in the pyroelectric image. The low pyroelectric activity of the spherulites indicates that these are flat-on lamellae with molecular chains oriented orthogonal to the sample surface.

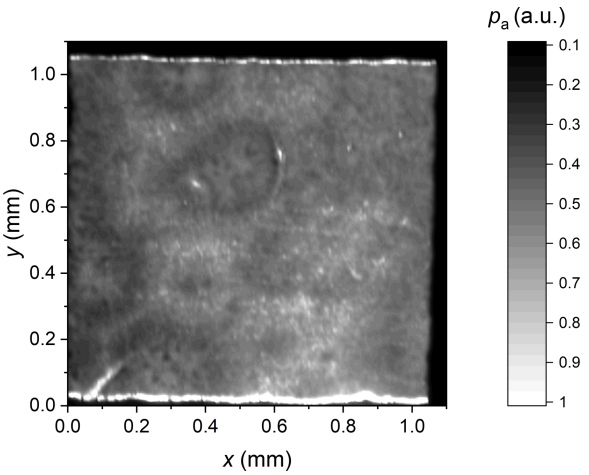

Fig. 5. Pyroelectric image of sample D62f. Dark colour indicates low and white colour high pyroelectric activity.

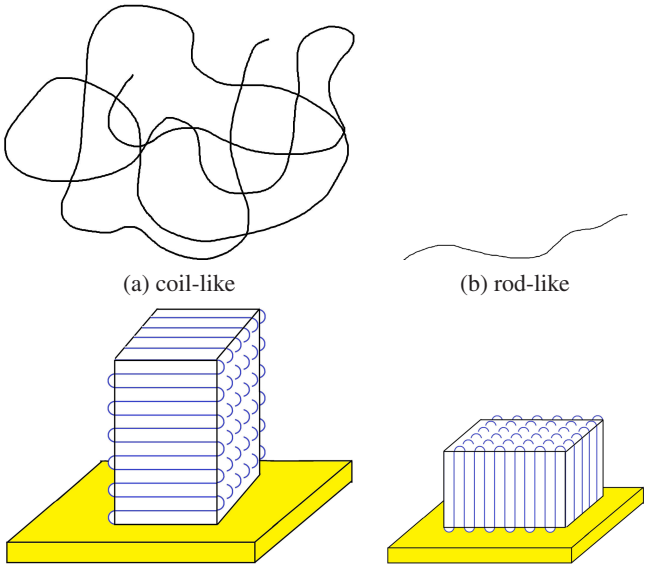

Fig. 6. Illustrations of (a) coil-like and (b) rod-like polymer configuration in solution. Illustrations of (c) edge-on and (d) flat-on crystallite orientation on a substrate.

4. Conclusion

When VDF-TrFE copolymer film is heated above the melting temperature after deposition on a substrate by spin coating the resulting structure and ferroelectric properties are very different for film fabricated from filtrated or from unfiltrated solution in MEK.

Film fabricated from filtrated solution shows strong growth of spherulitic lamella and low remanent polarization below 4 μC/cm^2. Pyroelectric images show that the spherulites have very small pyroelectric activity, i.e., they consist of flat-on lamella. This is also confirmed by X-ray diffraction measurements where the (200) + (110) reflection does not appear, but the (201) + (111) peak.

In contrast, no spherulitic lamella are growing in film fabricated of unfiltrated solution, and these show higher remanent polarization of 5.5 μC/cm^2. The (200) + (110) reflection is very strong, much stronger than in all films which had been annealed below the melting temperature only.

It is obvious that the filtration process has a strong effect on the structure of the deposited film which becomes visible when the film has been molten. An explanation for this observation is that filtrating changes the structure of the copolymer in solution from polymer coil to rod. Copolymer rods deposited on a substrate will crystallize in flat-on lamella when heated above the melting temperature, in contrast to copolymer coils which crystallize in edge-on lamella.

Illustrations of coil-like and rod-like polymer configuration in solution as well as edge-on and flat-on crystallite orientation on a substrate are shown in Fig. 6.

Further investigations of the effect of the filtration process on the structure control of the films are planned. In particular the effect of the pore size of the filter will be investigated.

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