Optical characterization of thin ferroelectric P(VDF-TrFE) films structural composition

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Introduction

The ferroelectric polymer material P(VDF-TrFE) is promising in terms of applications in such fields of technology as wearable medical electronics, tactile sensors, actuators, energy harvesting, and even nonlinear optical devices [[1]Z. Yin, B. Tian, Q. Zhu, C. Duan. Characterization and Application of PVDF and Its Copolymer Films Prepared by Spin-Coating and Langmuir–Blodgett Method. Polymers 2019, 11, 2033]. Among its advantages are flexibility, high chemical resistance and biocompatibility. Thin films are an important form of production this material for practical applications. Depending on the fabrication and operation conditions, this copolymer can exist in several polar and non-polar molecular conformations, or phases. The β-phase attracts the greatest practical interest in terms of ferroelectric properties. Different methodologies of such material fabrication are existing and continuing their development. Particularly, for film thicknesses above 10 nm, spincoating techniques can show good results.

Tasks

The aim of the work was fabrication of thin (about 200 nm) smooth P(VDF-TrFE) film, which would have β-type molecular configuration of polymer. Also to study the influence of thermal and flash-lamp annealing on obtained film`s properties.

Methodology

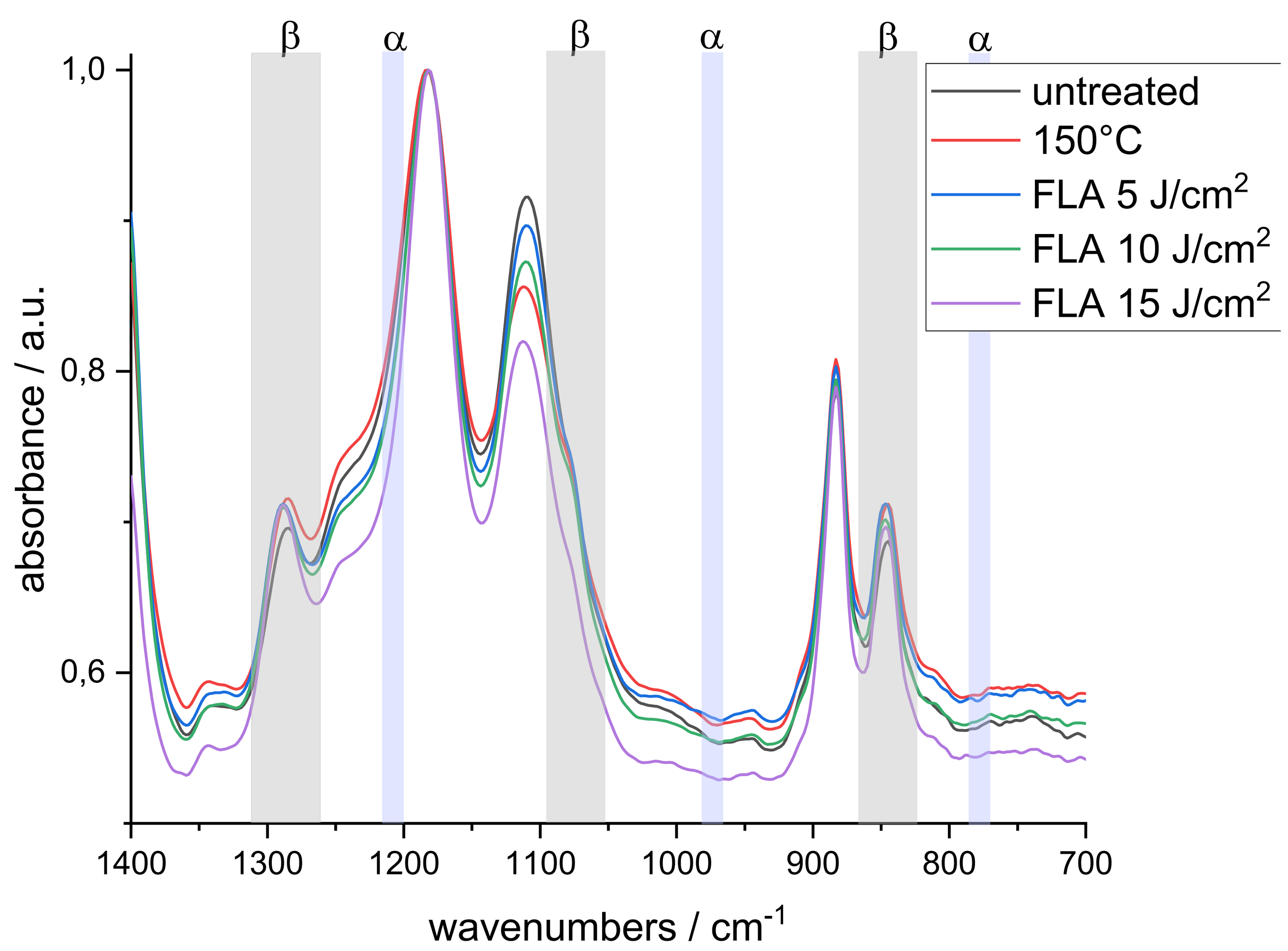
Thin films formation has been conducted using spincoating method. The initial solution was prepared of 25/75 mass molecular composition P(VDF-TrFE) copolymer powder dissolved in DMA. Different combinations of polymer in solvent concentration and substrate rotation speed were tested during the experiments to find the best film formation conditions. Further thermal annealing at 150°C temperature was applied to the films obtained, as well as flash lamp annealing (FLA) with 5, 10, and 15 J/cm^2 fluencies.
Films characterization was performed by atomic force microscopy (AFM), spectral ellipsometry (SE) RC2 ELLIPSOMETER, X-ray diffraction (XRD) and IR spectroscopy methods.

Results presentation

As a result of optimal conditions search for uniform polymer film formation, 7% mass P(VDF-TrFE) in DMA weight concentration and 7000 rpm baseplate rotation speed were chosen. A set of polymer-on-glass samples formed initially at these conditions was taken to estimate their film thicknesses and surface roughness using ellipsometrical one-layer model fitting and AFM data analysis. The samples were exposed to thermal and flash-lamp treatment with different temperatures and fluences. The results are presented in the following table:

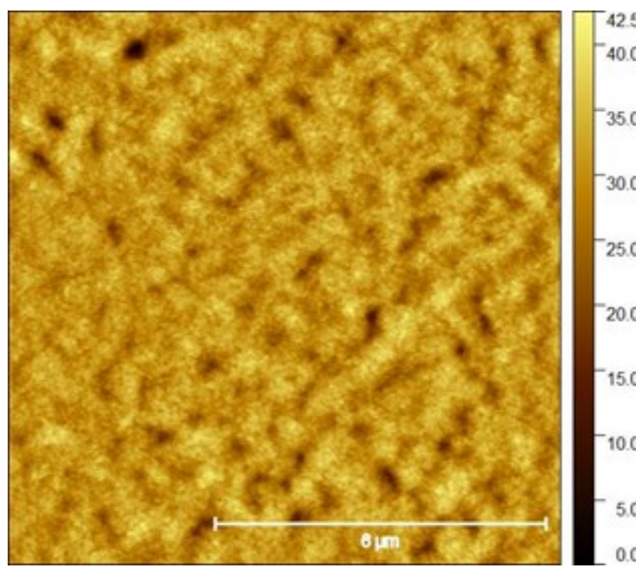
Table 1. Films thicknesses and surface roughness estimated by SE and AFM methods

Film	Thickness (nm)	Roughness (nm)	Roughness (nm) (AFM)
untreated	240,30	1,85	3,58
T = 150°C	232,65	8,80	10,76
FLA 5 J/cm^2	242,55	1,05	3,09
FLA 10 J/cm^2	255,00	0,85	3,08
FLA 15 J/cm^2	245,00	0,85	2,24

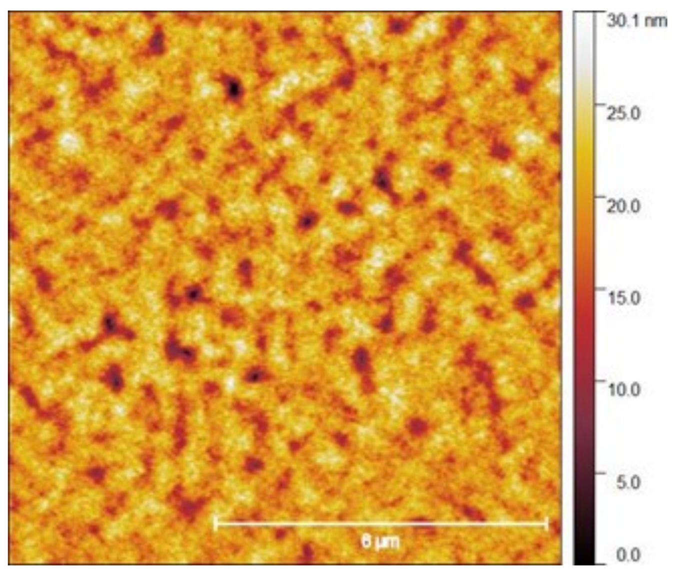


IR spectroscopy for thin films of P(VDF – TrFE)

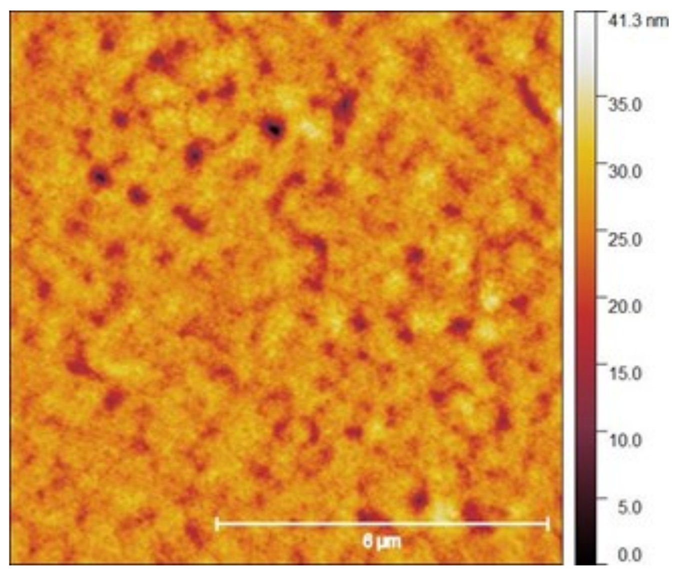
AFM images



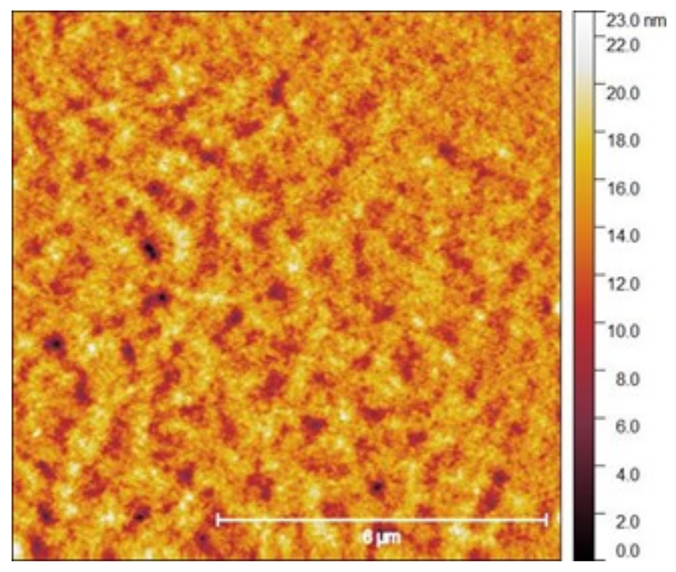
Untreated sample



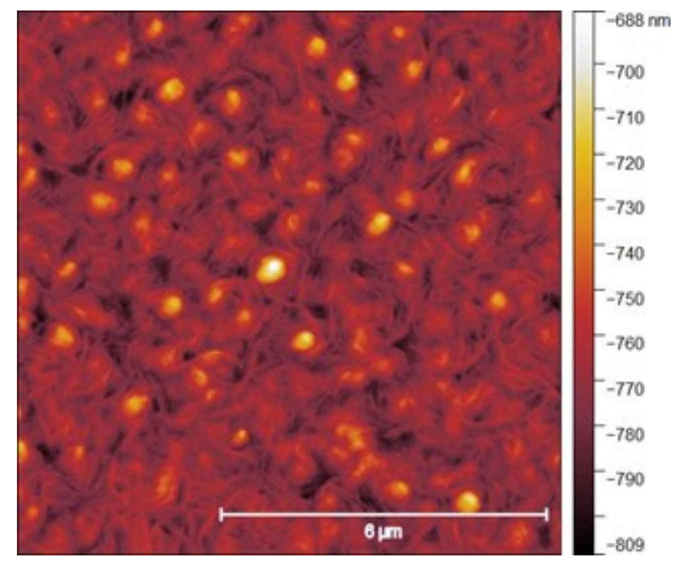
FLA 5 J/cm^2



FLA 10 J/cm^2



FLA 15 J/cm^2



T = 150°C

Conclusions

1. The methodology of 200 nm thick ferroelectric P(VDF-TrFE) film obtaining by copolymer solution in DMA spincoating was developed. Dominant β-phase composition of the film was verified by IR spectroscopy.
2. At right conditions, polymer film formed can have initially β-type predominant molecular conformation.
3. Further thermal or flash-lamp treatment makes influence mostly on its surface relief: the former increases surface roughness, the latter decreases it.