

Lamellae Orientation Effect on Local Polarized Domain in P(VDF/TrFE) Copolymer: Application in Data Storage

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ABSTRACT: In our previous article we achieved a high planar orientation of the poly(vinylidene fluoride and trifluoroethylene) [P(VDF/TrFE)] crystalline lamellae.¹ This short article focuses and reports our studies on the effect of this lamella orientation on its local polarized domains. Two samples A and B are considered in this investigation. In many parts of the film area, the lamella nanocrystals were oriented parallel to the substrate along a unidirectional axis by a newly conceived method, which consists of depositing a thin film on the clean surface of distilled water (sample A). In the second type (sample B), a film was prepared on highly oriented pyrolytic graphite (HOPG) by spin-coating, showing random and entangled lamellae in the amorphous phase. Atomic force microscopy (AFM) has been used to investigate morphological development and the local poled domain during an applied bias voltage for both A and B samples. The results showed that a minimum bias voltage of +3 V was enough to observe the local poled domain in the

case of oriented lamellae (sample A) while there was no piezoresponse measured in the case of random lamellae (sample B). When we increased the applied bias voltage, sample B showed a recorded local domain as a piezoresponse while in the case of sample A the local domain was enlarged. We can suggest that, during the preparation of sample A, the macromolecules had a preferential stable position where the dipole moments did not need a strong bias voltage to be switched but cross to the coercive voltage V_c . The character of oriented lamella nanocrystals can minimize the poling voltage in ferroelectric organic ultrathin films and will have an advantageous influence on production of a high-functionality mass memory device in data storage. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1410–1413, 2005

Key words: crystal structures; nanotechnology; atomic force microscopy (AFM)

INTRODUCTION

Ferroelectric organic films with a thickness in the nanometer range are one of the most interesting topics studied in the field of nanotechnology. Recently, a number of significant discoveries have been made in this field, for example, thin polymer films that display highly ordered patterns under strong electric fields² or rubbing induced orientation in the phase separation of ultrathin polymer blend films.³

A ferroelectric thin film can be locally poled by applying a pulse voltage higher than its coercive electric field between the conductive cantilever and the bottom electrode using the AFM contact mode (Fig. 1). Different areas in the film were poled by scanning the tip with a negative or positive dc bias voltage. In previous studies on data storage in organic materials, thin films of poly(vinylidene fluoride and trifluoroethylene) [P(VDF/TrFE)] copolymer memory bits have been written on using the local polarization induced by an electric field from a Scanning Probe Microscopy

tip.^{4–6} Previous studies have demonstrated that, for a mole fraction of VDF between 54 and 82%, the P(VDF/TrFE) copolymer presents exclusively specific features and ferro- and nonferroelectric properties. The copolymer has a semicrystalline structure: small crystals are embedded in an amorphous matrix. These small crystals are responsible for the ferro-, piezo-, and pyroelectric properties of the material. The morphology of this copolymer is that of a long macromolecule in a *trans* conformation as presented in Fig. 2, where the unit cell contains VDF ($-\text{CH}_2-\text{CF}_2-$) and trifluoroethylene TrFE ($-\text{CF}_2-\text{CFH}-$). It may be noted that the macromolecular character of these molecules is particularly advantageous because it suppresses complicated fluctuation.⁷ The difference in electronegativity between fluorine and hydrogen atoms results in randomly oriented dipole moments. Consequently, under applied dc voltage, the dipoles can be switched, but unfortunately the mechanism of reorientation of dipole moments is not well known. It was demonstrated by Kajiyama et al.⁸ that, after applying a strong electric field, the dipole moments were not reoriented completely parallel to the electric field but few dipoles were deviated in the Gaussian distribution. However, the determination of the orientation angle of these dipoles is still difficult and ambiguous

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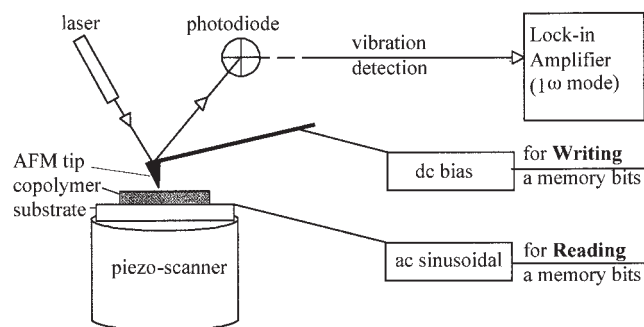


Figure 1 Schematic illustration of visualization of poled local domains in ferroelectric films using Scanning Force Microscopy. Both piezoresponse and topographic images were taken simultaneously.

even using the Scanning Maxwell Stress Microscopy (SMM).

This article deals with a structural investigation of the P(VDF/TrFE) ultrathin film copolymer and its ferroelectric properties. The intention was to study structural changes induced by a new method of fabricating a unidirectional oriented crystalline lamella on the local polarized domains.

EXPERIMENTAL PROCEDURE

The P(VDF/TrFE) 73/27 powder was dissolved in methyl-ethyl-ketone (MEK). Good compatibility between this copolymer and the MEK solvent aids the formation of a monophasic. Other solvents such as cyclohexanone would be less suitable because complete miscibility does not exist between copolymer and solvent. In this study, we present two different methods to obtain an ultra-thin film copolymer and thus two different samples: A and B.

In method A, the clean surface of distilled water was used as an intermediate substrate. In this way, a drop of copolymer solution was immediately spread by hydrodynamic flow over the whole surface of the beaker. The thickness was controlled by the weight concentration of copolymer in solution and the dimensions of the water surface. The deposited film was picked up on a highly oriented pyrolytic graphite (HOPG) substrate. The whole procedure was performed in a clean room to prevent contamination.

To obtain sample B, the well known spin-coating method was used. The samples were spin-coated onto a HOPG substrate with a rotation rate of 3,000 rpm for a few seconds at room temperature. The average film thickness for both samples was about 30 nm, as measured from the AFM line profile. Both samples A and B were annealed in a vacuum at 140°C for 2 h. This increases the crystallinity of the copolymer films as discussed in previous papers.⁹

Surfaces structures were investigated using the atomic force microscopy (AFM). A standard setup of the AFM combined with the lock-in amplifier was used to detect the cantilever deflection for obtaining topography images and to visualize the polarized domain as piezoresponse images. For determining the local ferroelectric polarity and domain structure directly, we measured the strain of the thin-film copolymer caused by an applied voltage to this film through the AFM cantilever tip. The oscillating voltage caused the mechanical oscillation of the film and thus the cantilever due to the contact mode of AFM where the cantilever tip is in contact with the copolymer film surface. The film copolymer vibration is detected by a photodiode and then by the lock-in amplifier, in which the output signal provides information such as the phase of signal, time constant, and change in the film thickness at any instant of the vibration. The phase of the output signal depends on the polarization direction, i.e., depending on the state of the grains in the lamella. When the polarity of applied voltage changed, the grains of lamella were compressed or expanded and thus the phase changed [4,5,10,11]. Consequently, a piezoelectric image could be taken, which shows the poled and unpoled domains.

RESULTS AND DISCUSSION

Figures 3 (A1; and B1) show the AFM images of structures of the two P(VDF/TrFE) copolymer films and in both cases show lamellar or rod-like structures but with different textures in each case. In the case of sample A, the lamellae have an ordered and oriented texture parallel to the HOPG substrate as shown in Fig.3(A1). In contrast to this, the use of the spin-coating method for sample B leads to a random mixture and entanglement of lamellae as shown in Fig.3(B1). This is clearly independent of the substrate, as the same substrate was used in both cases.

To explain this behavior in sample A, it is suggested that the morphology in sample A is the result of the

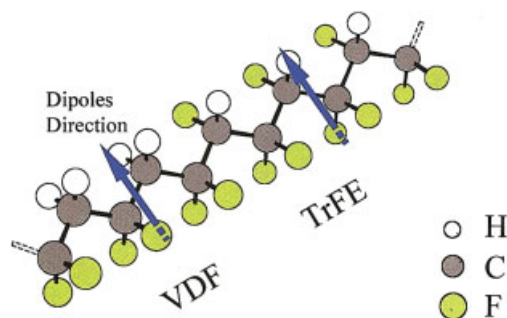


Figure 2 Schematic drawing of the molecule chain *trans* conformation in P(VDF/TrFE) copolymer. The arrow shows the dipole direction resulting from the difference in electronegativity between fluorine and hydrogen atoms.

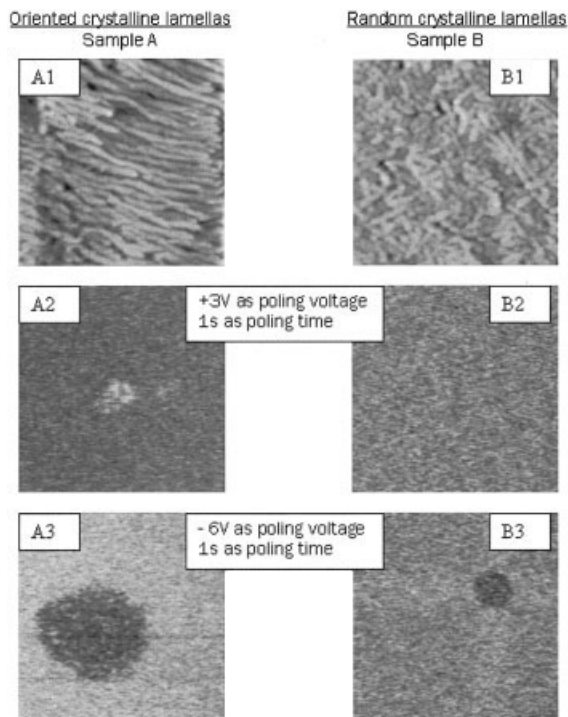


Figure 3 (A1, B1) Topographic images respective to A ($2\ \mu\text{m} \times 2\ \mu\text{m}$) and B ($4\ \mu\text{m} \times 4\ \mu\text{m}$) samples. (A2, B2) Piezoresponse images showing the local switched domains formed in P(VDF/TrFE) copolymer in A and B samples, respectively, under $+3\ \text{V}$ as positive poling voltage. (A3, B3) Piezoresponse images showing the local switched domains formed in P(VDF/TrFE) copolymer in A and B samples, respectively, under $-6\ \text{V}$ as negative poling voltage.

slow spreading of the crystalline lamellae on the water surface under the effect of hydrodynamic driving force flow. The hydrodynamic force allows the formation at an unidirectionally ordered structure. The impact of the copolymer solution drop on a water surface was governed by a slow growth velocity and lamellae had a preferential unidirection arranged parallel to the substrate. It is noted, however, in some parts of sample A the lamellae were randomly dispersed. This process is still, however, not well understood or easily controllable and is under further investigation.

In sample B, the orientation of lamellae is in a random state. The width of lamellae is about $100\ \text{nm}$ and the length is about several hundred nanometers depending on the annealing conditions.

In the oriented part of sample A an interesting behavior under the bias electric field was observed. The piezoelectric response of both samples A and B was measured by applying a bias dc voltage between the gold-coated cantilever and the conductive substrate. The applied dc voltage or poling voltage served to switch the dipole moments and thus polarize samples while the ac voltage can read and thus show the piezoelectric response. In another way, the continuous electric current (dc) was used to create local polarized

domains while the alternative current (ac) was used to visualize these domains. The polarized domains were obtained after switching the dipoles using an applied electric field to the copolymer film. The dipole moment directions are oriented in the same direction as the electric field vector. The changing direction of the switched dipole moment has an effect on the changing phase of the signal. If the dipoles in copolymer film are in random orientation there will be no change in the phase and then no piezoelectric response can be observed. Only a polarized domain could be detected by the lock-in amplifier and be visualized in the piezoelectric image by the difference of contrast. The colors in the piezoelectric images shown in Figs.3(A2, A3, and B3) distinguish between poled and unpoled domains.

Figure 3(A2) shows local domains that were polarized by a positive poling voltage of $+3\ \text{V}$ to sample A. Therefore, a recording mark (yellow color) as a pattern domain with a diameter of approximately $100\ \text{nm}$ was written in sample A. The same poling voltage had no effect on sample B and could not switch the dipole moments, and thus no piezoresponse was revealed. The poling time, i.e., the duration of the pulse voltage, was kept constant for both cases and evaluated at $1\ \text{s}$. The writing speed and the reversibility parameters are not treated in this short article. When we increased the poling voltage to $-6\ \text{V}$, sample B in Fig.3(B3) showed a recording mark (brown color) as a piezoresponse while in sample A the mark diameter shown in Fig.3(A3) was enlarged to $400\ \text{nm}$ approximately. We noticed that the change in color from yellow to brown resulted from the phase change, which is due to the sign of the applied voltage. It is suggested that in sample A the macromolecules were suitably oriented so that the dipole moments did not need a strong bias voltage to be switched. This behavior could be explained by the low contact area between lamellae, which can reduce the electrical interaction and the mechanical tension stress between macromolecules. Thus, the dipole moments can be more easily switched in sample A than sample B.

The control over the microscopic and macroscopic orientation of these structures in thin films may lead to many applications of ferroelectric copolymers in nanotechnology. In addition, it is hoped that the use of novel detachment replication techniques in conjunction with electron diffraction will provide complementary information concerning the changes in the local molecular orientation that occur within lamellae.

CONCLUSION

The development of a methodology to control the lamellar structure of poly(vinylidene fluoride and trifluoroethylene) copolymer on nanoscopic scales together with the resulting effect on the piezoresponse

has been the focus of this investigation. A new film deposition method using the clean surface of distilled water was employed to produce a thin film with good alignment of crystalline lamellae by hydrodynamic flow. This orients the macromolecular chains in one direction. The effect of an electric field on this oriented structure reorients most dipole moments in the direction perpendicular to the HOPG substrate. It was demonstrated that the local polarized domains are highly dependent upon the ordering of the lamellae.

Highly oriented lamellae result in a minimization of the poling voltage in ferroelectric organic ultrathin films and could therefore find an application in high-functionality mass memory data storage devices.

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