Annealing Effect on Poly(vinylidene fluoride/trifluoroethylene) (70/30) Copolymer Thin Films Above the Melting Point

Weiping Li, Lijia Yu, Yuejin Zhu, Dayin Hua, Jun Wang, Laihui Luo, Jing Zhang

Department of Physics, Ningbo University, Ningbo 315211, China

ABSTRACT: To further understand crystallization behaviors above the melting temperature (T_m), the morphologies and structure of ferroelectric poly(vinylidene fluoride/trifluoroethylene) [P(VDF–TrFE); 70/30] copolymer films at different temperatures were studied by atomic force microscopy, differential scanning calorimetry, and X-ray diffraction (XRD). We found that there was a structural change in the P(VDF–TrFE) copolymer film above T_m, which corresponded to the transition from tightly arrayed grains to fiberlike crystals. For the samples annealed above T_m, heat treatment reduced the density of gauche defects and caused a better arrangement of the crystalline phase. So those samples were in the ferroelectric phase without gauche defects, with one sharp diffraction peak reflected in the XRD curves. It was helpful to further make clear the thermal behaviors from the melts of the P(VDF–TrFE) copolymers and discuss their application under higher temperatures. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 663–667, 2010

Key words: annealing; atomic force microscopy (AFM); X-ray

INTRODUCTION

Poly(vinylidene fluoride/trifluoroethylene) [P(VDF–TrFE)] copolymers, containing vinylidene fluoride in amounts between 55 and 82 mol %, have been widely studied during recent years for their interesting properties, including their piezoelectric, ferroelectric, thermoelectric, and electrostrictive properties.[1–3] These polymers can crystallize into four types of crystals forms: form I (β), form II (α), form III (γ), and form IV (δ). Among the four types, only the β phase is the polar ferroelectric phase consisting of all trans chains, and the other three phases are nonpolar phases consisting of Trans-Gauche (TG or TG′) conformations.[4]

It is well known ferroelectric properties originate from the crystalline region and are strongly influenced by higher order structures, such as the degree of crystallinity, orientation, and crystal size in the samples. Although annealing treatment is an effec-

tive method to obtain a high crystallinity, many studies have been reported an annealing effect on P(VDF–TrFE) copolymers.[4–6] However, most studies have been focused on the effect of the annealing temperature in the range of Curie (T_c) and the melting temperature (T_m). Furthermore, the corresponding thermal behaviors above T_m have often been neglected. Although a few studies concerned about the recrystallization effect on P(VDF–TrFE) copolymers above T_m have been reported recently,[7–10] the thermal behaviors above T_m are not yet clearly understood, and further studies are still necessary.

On the other hand, with the development of scanning probe microscopy technology, it is possible to study the microstructure and orientation mechanisms of P(VDF–TrFE) copolymers. For the first time, Guther and Dransfeld[11] advocated that it is possible to control and image local polarized domains on P(VDF–TrFE) copolymer thin films by atomic force microscopy (AFM). Yamada and coworkers[12–14] further reported the substrate effect, local structures electrical properties, and orientation control of P(VDF–TrFE) films by AFM. Afterward, more studies on the microstructures and properties of P(VDF–TrFE) thin films were carried out.[15–17] Recently, Wi et al.[10] analyzed P(VDF–TrFE) (50/50) thin films at temperatures of 70–200°C and found that those films annealed at 200°C showed rougher surfaces. However, in their study, there were no detailed results in the range from 150 to 200°C. The T_m of those samples in their study was 158°C, and it

was not enough to interpret the characterization above T_m. In a previous study, we found that P(VDF–TrFE) (70/30) copolymer films exhibited a great transition in morphology above T_m.[18] Here, the gradual transition of morphology with annealing temperature (T_a) was present directly, as observed by AFM, and we aim to make clear the annealing effect within a broad temperature range. It will be helpful to make clear the microscopic mechanism and thermal behaviors under different crystallization conditions and to further discuss their application at higher temperatures.

EXPERIMENTAL

P(VDF–TrFE) (70/30 mol %) was obtained from Piezotech in Hésingue, France, in the form of white pellets. These pellets were dissolved in dimethylformamide by stirring at room temperature (T_R). Thin films were then formed by solution casting on mica flakes. Because the density of the copolymer was a fixed value, the thickness of films could be influenced by the concentration, volume of solution, and area of substrate. Here, the concentration was 1 mg/mL, and the area of the mica flakes was about 1×1 cm^2. Thus, the thickness of the films could be controlled by the volume of solution. Generally speaking, 0.9 mL in volume corresponded to 5 μm in thickness. The copolymer films were annealed at different temperatures for 2 h and cooled to T_R in 1 h. The temperature program was controlled by chamber SU-261 (ESPEC Corporation, Japan).

To be propitious to AFM measurement, the samples were deposited on mica substrate with a thickness of 5 μm. Then, the films were taken off of the mica for X-ray diffraction (XRD) or differential scanning calorimetry (DSC) measurement. The pictures of the samples' surfaces were obtained with a NanoScope III multimode scanning probe microscope (Veeco Instruments, USA) at T_R. XRD was carried out with a Philips Dual X'Pert XRD system (PANalytical Corporation, Netherland) with Ni-filtered Cu Kα radiation at a scanning speed of 0.005° 2θ/s. DSC was performed with a PerkinElmer (USA) Sapphire DSC thermal analyzer at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The AFM images of the bare mica substrate and annealed P(VDF–TrFE) at different T_a values are shown in Figure 1. As shown in Figure 1(a,b), the bare mica substrate had a smooth surface, and the topography of the unannealed sample was full of tiny grains with an average size of about 20 nm long and 10 nm wide. Comparing these three images, we found that the P(VDF–TrFE) copolymer film did not follow the morphology of the mica surface. As shown in Figure 1(c), the crystalline grains arrayed

tightly and orderly on the surface of the 120°C annealed sample with an average size of 80 nm long and 40 nm wide. With increasing T_a, the grains enlarged gradually, and their sizes were up to 210 nm in length and 120 nm in width for the 145°C annealed sample. The T_m of the P(VDF–TrFE) copolymer in this study was approximately 150°C. Therefore, after crystallization in the range from a certain temperature below T_m to T_R, the P(VDF–TrFE) copolymers were in the ferroelectric phase with many large domains. When T_a was increased to 148°C, the crystalline grains continued to enlarge, and the neighboring ones were united into rods 700 nm long and 150 nm wide; this result was also reported by other authors.[13,17,19] When T_a was above T_m, because of the increasing flexibility of the chains, more and more grains came together to combine, and the rods became long and straight. When T_a was up to 160°C, higher than T_m, the rods got longer, and finally, the topography exhibited a bird's nest type, which consisted of randomly oriented long fibers. For the 170°C annealed sample, the average size was 3 μm in length and 200 nm in width. According to Bassett's study,[20] the straight rods here were fiberlike crystals consisting of extended chains, and the extended direction of the chains was parallel to the outspread fiberlike crystals. As shown in Figure 1, the data scale of height of the 160°C annealed sample was up to 300 nm, about six times that of the 140°C annealed sample. This indicated that the thickness of the fiberlike crystals increased with increasing T_a, and this may have corresponded to the rough surface in Wi et al.'s[10] AFM study.

On the other hand, Sasaki et al.[21] demonstrated that P(VDF–TrFE) copolymers films were composed of stacks of thin and thick lamellae with respective widths of 8.5 and 57 nm in the range 25–147°C and were composed of only thick lamellar stacks in the range 155–165°C. Because of the melting of crystals, the thin lamellar stacks disappeared in the range 147–155°C. This indicates that the starting point (147°C) of structural change was accordant with our results (148°C here). We believe that there must be a relation between those lamellar stacks and our rod structures. Also, we concluded that there was a structural change in the P(VDF–TrFE) copolymer film above T_m corresponding to the transition from tightly arrayed grains to fiberlike crystals.

Figure 2 shows the DSC curves under different T_a's. The peak at the lower temperature (T_c) in all of these curves was associated with the ferroelectric to paraelectric (F-P) phase transition in the crystalline regions, whereas the one at the higher temperature (T_m) reflected the melting behavior of the crystalline regions in the materials.[22] With increasing T_a, the peaks of both T_m and T_c shifted to higher temperatures. The increase of T_c was most possibly due to a decrease in the gauche defect density. Also, the shift
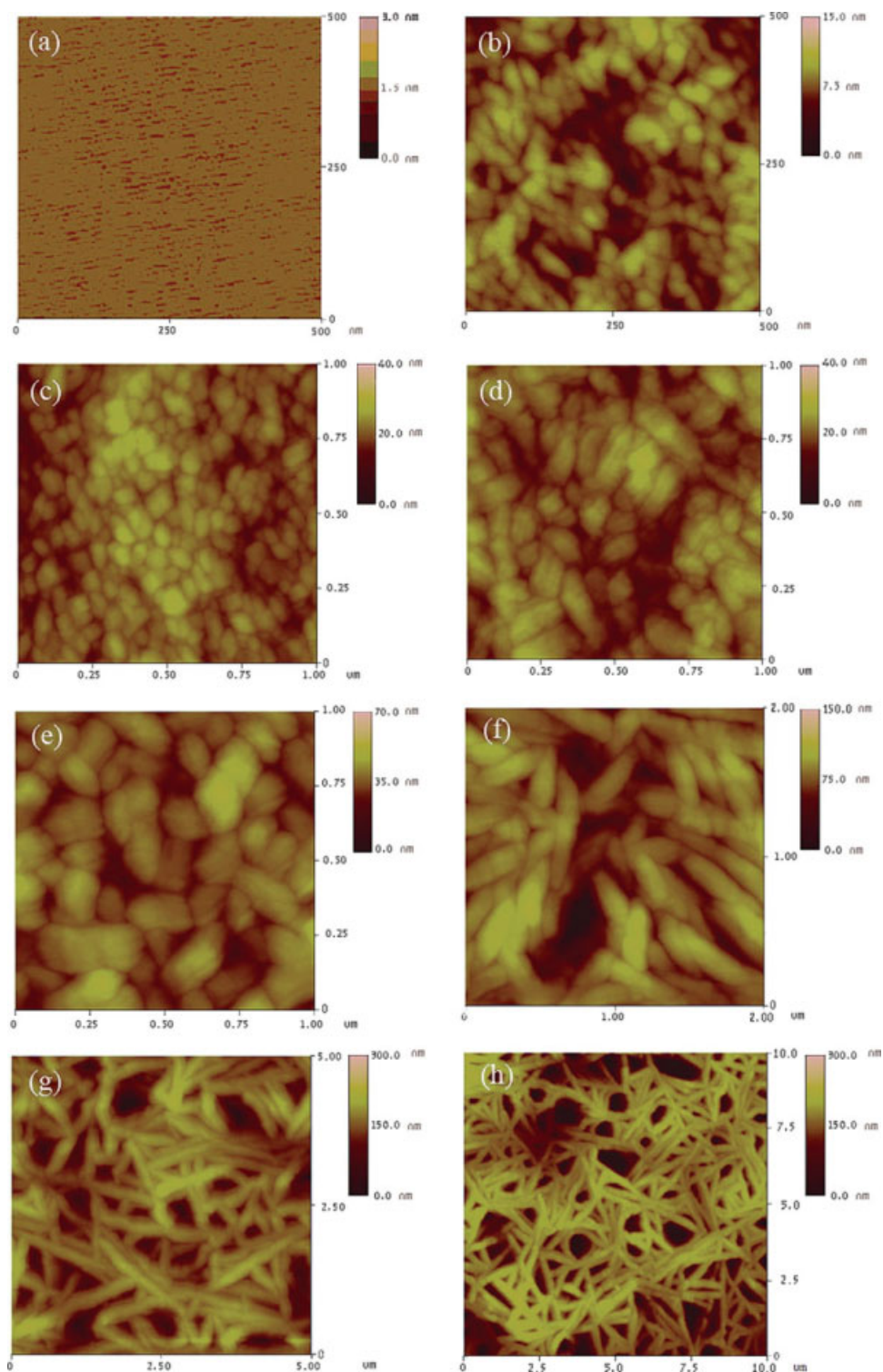
Figure 1 AFM images of the bare mica substrate and annealed P(VDF–TrFE) copolymer films at different temperatures: (a) bare mica, (b) untreated copolymer film, and copolymer films treated at (c) 120, (d) 140, (e) 145, (f) 148, (g) 160, and (h) 170°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

in T_m indicated a better arrangement of the crystalline phase because the chain molecules became very mobile along the chain axis.

X-ray curves of the samples annealed at different temperatures are presented in Figure 3. The reflec-tion at $2\theta = 19.7°$ was from the ferroelectric β phase and represented the Bragg diffraction of (110)/(200). The reflections at 17.7 and 26.8° were from the Bragg diffractions of (100) and (021) of the nonpolar α phase, respectively.[23] The intensities of the peaks at

17.7 and 26.8° decreased with increasing T_a and finally disappeared in the 160°C annealed sample, but that of the peak at 19.7° got sharper and stronger. The decrease in the nonpolar α phase with increasing T_a was accordant with the results of Wi et al.'s[10] study. However, in this study, the volume of the ferroelectric β phase simultaneously increased with T_a. This indicated that the Trans-Gauche (TG) sequences were replaced by all-trans sequences with increasing T_a. So the P(VDF–TrFE) (70/30) copolymer films crystallized at 120 and 140°C exhibited paraelectric phases and changed into ferroelectric phases during cooling to T_R, in agreement with the result of AFM. However, the ferroelectric phase corresponding to the all-trans conformation was an organized one with many gauche defects. Also, annealing above T_m reduced these gauche defects, which reflected the increase in the ferroelectric peak and the disappearance of the diffraction peaks from the nonpolar phase. So the P(VDF–TrFE) copolymer films after annealing above T_m were in ferroelectric phases without defects and reflected on only one sharp peak in the XRD study.

CONCLUSIONS

In this study, the annealing effect on P(VDF–TrFE) (70/30) copolymer films in a broad temperature range was examined. The gradual transition in morphology was examined directly by AFM. With increasing T_a, the increscent crystal grains were united into rods composed of fiberlike crystals. Also, the P(VDF–TrFE) copolymer films annealed in the range between T_c and T_m were in the ferroelectric phase with many gauche defects. However, anneal-
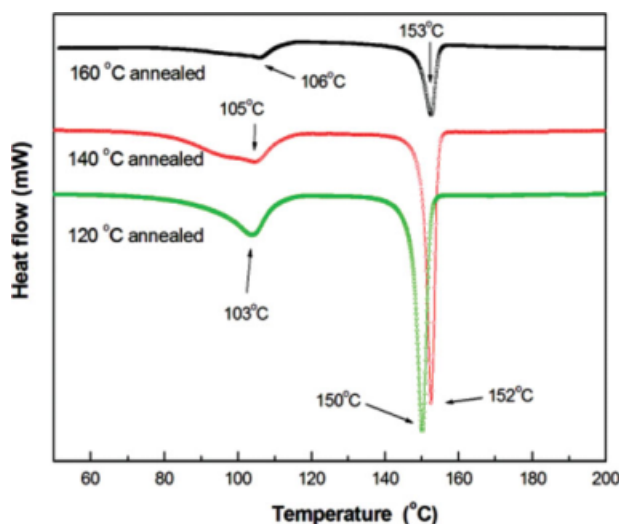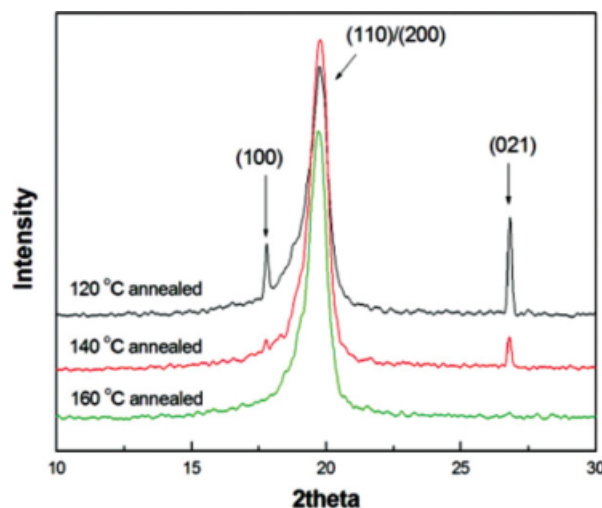

Figure 3 XRD curves under different T_a's. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ing above T_m introduced these defects into the all-trans sequences.

In this study, we examined only the annealing effect of 5 μm thick P(VDF–TrFE)(70/30) copolymer films prepared on mica flakes. The substrate effect, size effect, and differences in the vinylidene fluoride content were considered in this study. However, our results do indicate the structural changes in P(VDF–TrFE) copolymer films above T_m. They are helpful for further understanding the crystallization behaviors from the melts of P(VDF–TrFE) copolymers.

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Figure 2 DSC curves under different T_a's. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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