Electric Field–Induced Surface Morphology in a Copolymer of Vinylidene Cyanide and Vinyl Acetate

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We investigated the surface morphology of the film of a copolymer of vinylidene cyanide and vinyl acetate, using atomic force microscopy. It was found that when a high electric field is imposed to the film near its glass transition temperature, a thin fiber-like assembly about 10 nm thick appears on the surface. The surface structure was discussed relating to the relatively high piezoelectricity in this amorphous-type polymer.

A copolymer of vinylidene cyanide and vinyl acetate, called (P(VDCN/VAc)), shows a piezoelectricity that is stable when the polymer is below its glass transition temperature (Tg) of 170 ℃.[1-3] By imposing high direct current (dc) electric fields onto the film (poling) near the Tg, its cyanide groups with a large dipole moment are oriented and the film develops piezoelectric properties.[2] The stable orientation of the cyanide groups having a chemical activity is unique in piezoelectric polymers and is much important in terms of developing functions of film surfaces. From the point of view we investigated the surface of the P(VDCN/VAc) film and its behavior under electric field by using atomic force microscopy (AFM). It is an amorphous-type film, which has been indicated by the observations of no melting point and the broad X-ray diffractions.[4, 5] We discovered that in the amorphous-type film the surface structure of thin fibers type appeared after poling.

The P(VDCN/VAc) powder synthesized by radical polymerization[6] was dissolved in dimethylformamide (DMF) to provide a polymer concentration of 2.8%. The polymer solution was then cast onto flat glass plates. The samples were dried in an oven of forced convection type at 85 ℃ for 15 h. To remove the remaining DMF, the cast films were first washed several times in methanol using ultrasonic agitation and then dried. We divided each film into four pieces, which we then sandwiched between aluminum-film electrodes as shown in Figure 1. By simultaneously poling all four films, we could use films b and c to investigate surfaces apart from electrodes, and films a and d to investigate surfaces touched with electrodes. We used a dc power supply (Glassmann PS/ER06R) to apply a high electric voltage (electric field strength of 113 kVcm^{-1}) to the films at 169 ℃ (near Tg) for 30 min. The surfaces were examined using AFM (SFA-300, Seiko Instruments Co., Ltd.) with silicon cantilevers (spring constant of 14 Nm^{-1}) and in the tapping mode (resonance frequency of 120 kHz). A strongly tapping mode (a decrease rate of amplitude: 40-50%) was adopted to prevent the effect of long-ranged electrostatic force of the polar film in the scanning of the AFM tip. All of the AFM measurements were conducted after a suppression of an electric charge effect by fully exposing the films to air having moisture. Reproducibility was fully ascertained.

Piezoelectric strain constants d_{31} of the poled films a (near negative electrode), b, c, and d (near positive electrode) at 10 Hz were 0.64, 0.54, 0.66, and 1.45 pCN^{-1} respectively. For the d_{31}, the order of the films was $a \sim b \sim c < d$. Figure 2 shows the effects of poling on the surface morphology. (Note that all surfaces are the same air surfaces at casting.) The surface after casting (Figure 2(a)), but before poling, was slightly rough. After poling, the surface of the films that were not touching the electrodes (films b and c) contained curved, intertwined fiber-like assembly (Figure 2(c)). The assembly is thin, of which width distribution ranges from 8 to 21 nm. The assembly is field-induced, because the surface of film annealed at the same temperature and for the same time, but under no electric field (Figure 2(b)) contained random particles (diameters ranged from 25 to 65 nm) rather than fibers type. Surfaces of the films onto which the same strong field was imposed for the same time, but at room temperature and 100 ℃ revealed no fiber-like assemblies. In Figure 2(c) there are many fiber-type assemblies each of which has a few branches, and in some regions an assembly ducks out of other assembly. Figure 2(c) shows relatively clear images but there are also regions with no sharply outlined images after poling. After keeping the poled film at room temperature under air for 6 days, the image of fiber type is almost extinguised and is changed into that of unclear protuberances (Figure 2(d)). When the film getting the relaxation of the surface structure is exposed to the treatment of poling in the same condition as the first, a morphology of thin fibers type appeared again (Figure 2(e)). In the second appearance the width of the fiber-like assembly is slightly thicker and its length between junctions is shorter than those of the first assembly. The second one is a little more roundish. The surfaces of the films that touched the electrodes (films d and a) after the first poling showed protuberances rather than fibers type (images are not shown here.).

Fiber-like morphology was seen on inner surfaces apart from electrodes at poling. The surface of film d (near the positive

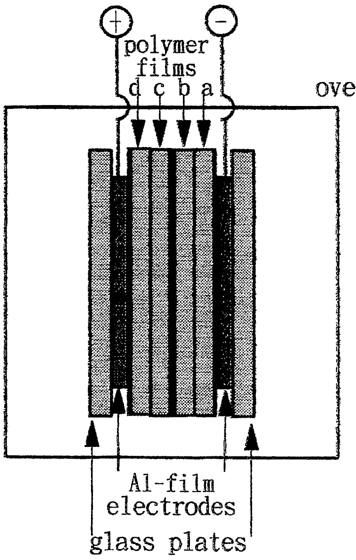

Figure 1. Polarization of P(VDCN/VAc) films. Thick lines on the polymer films are the air surfaces. Film thickness is 75 μ m.

electrode) revealed a morphology of a mountain range with a diameter of 20 to 70 nm. The surface of film a (near the negative electrode) revealed that of relatively unclear protuberances.

Since the discovery of this piezoelectricity about 15 years ago, the structure and electrical properties of this polymer have been extensively studied.[1,2,5-16] From the behaviors of the broad low-angle diffraction patterns at $2\theta = 15^\circ$ and 30° and the large dielectric relaxation (more than 100) above Tg it has been suggested that it might form a phase with significant intramolecular interactions.[7,8] In this letter we report the field-induced "meso-assembly" in amorphous polymer. The appearance of fibers-type assembly 10 nanometer thick on surface strongly suggests that the assembly is composed of numbers of chains aggregating in relative parallel with such intramolecular interactions. The partial relaxation of the assembly seems to occur in day-scale. After the relaxation the treatment of repoling recovered meso-assembly but slightly different from the first. On the other hand, piezoelectric constant keeps constant more than one year after first poling.[3] If the meso-assembly is an origin of the large piezoelectricity for amorphous type, the relaxation may occur in only the vicinity of surface. In addition, the surfaces touched with electrodes showed no characteristic assembly. The "meso-assembly" would not have been found in a conventional system of one-film poling. Maybe, it is sensitive to surface condition. As its reason, an effect of aluminum film or charge injection from electrodes is thought. The latter induced inequality of piezoelectric constants of four films.[17,18] The appearance of the assembly resembles that of lamellae in a crystalline piezoelectric polymer, vinylidene fluoride-trifluoroethylene copolymer.[19] However, from previous analyses of P(VDCN/VAc) it should not be lamellae crystallite. We will conduct further experiments to clarify the properties of the assembly.

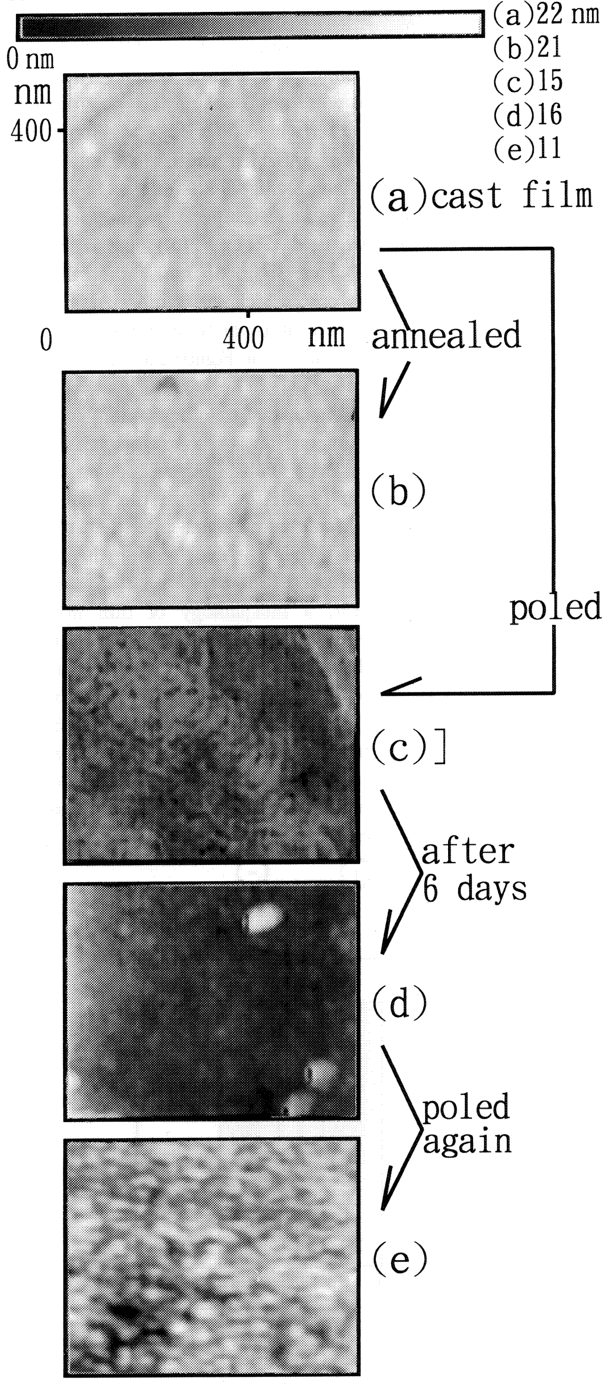

Figure 2. AFM images of P(VDCN/VAc) films (air surface). (b), (c) and (e): at 169 ℃ for 30 min. From (c) to (d): kept at RT in air.

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References and Notes

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