Electrical Conductivity in Nylon 66 Thin Films Prepared by Alternating Vapor Deposition Polymerization

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ABSTRACT : Electrical conductivity of Nylon 66 thin films prepared by alternating vapor deposition polymerization (AVDP) and interfacial polymerization (IFP) were measured as a function of temperature and humidity. AVDP films had highly ordered structures with the molecular orientation normal to the substrate with the tilting angle of about 54°. Electrical properties of AVDP and IFP films were made along the film thickness direction and parallel to the film surface. The conductivity of AVDP film was anisotropic over temperature ranges of 50–200°C. The conductivity of AVDP film perpendicular to the film thickness was larger than that along the film thickness direction. Temperature dependence of the conductivity showed three temperature ranges: ① below T_g , ② $T_g \sim 100^\circ\text{C}$, ③ above 100°C. The activation energy for the conductivity decreased with humidity in the range of $T_g \sim 100^\circ\text{C}$ but was almost constant above 100°C. Carriers were supposed to be impurities, such as hydrochloric acid in AVDP films and sodium chloride in IFP films. The ionic jump distance was estimated to be about 3.5 nm above T_g .

KEY WORDS Electrical Conductivity / Anisotropy / Nylon-66 / Vapor Deposition / Humidity /

Electrical conductivity for hydrogen-bonded polymers such as nylons, cellulose and polypeptide, has been studied by many workers^{1–6} in order to clarify whether charge transfer involves the transport of ions or electrons. Eley et al.¹ reported an amide-proton as a charge carrier. Seanor⁴ proposed a protonic conductivity above 90°C detecting H₂ gas evolution under a DC field and an electronic conduction below 90°C because of no evolution of H₂ gas. Saito et al.⁵ adopted an ionic conduction based on a pressure dependence of the conductivity at 22–115°C and proposed a proton transfer through a hydrogen bonded network. Miyaji et al.⁶ found three temperature ranges on temperature dependence of the conductivity of nylon-66: ① below 97°C, ② 97–250°C, ③ above 250°C, and proposed an ionic conductivity based on impurity ions but not amide protons. According to these experimental data, it could be concluded that the ionic conduction takes place in hydrogen-bonded polymers even in a conventional dry state since a trace of water contains in samples which plays an important role in a charge transport mechanism.

On the other hand, morphological views in the conduction mechanism are also very important: conducive region is whether a crystalline or amorphous region, charge transfer involves whether intermolecular transfer or intramolecular transfer and whether parallel to the chains of hydrogen bonds or perpendicular to the sheets of hydrogen bonded molecules. Charge transfer of ion and adsorption of water in hydrogen-bonded polymers take place in an amorphous region rather than in a crystalline region⁶. A few works have been reported in doubly oriented nylons^{3,7}. Doubly oriented nylons showed that the conductivity was anisotropic over a wide range of temperature, being least along the chain axis and greatest along the hydrogen-bonded planes. More details in the morphological effects require a defined structure. Large single crystals of polymers are preferable to clarify the morphological effect on the conductivity but they are impossible to obtain.

Vapor deposition polymerization (VDP) is a useful and promising method for producing functional polymeric

thin films with thermal stability such as polyimide thin films^{8,9}, and producing high performance polymeric thin films such as polyurea films having piezoelectricity and pyroelectricity¹⁰. This method also gives the molecular orientation in a polymeric thin film. For example, nylon-1010 films having normal molecular orientation on the substrates are obtained by the VDP method¹¹.

In the alternating VDP (AVDP), two kinds of bifunctional monomers, such as an adipoyl chloride monomer (ADC) and a hexamethylene diamine monomer (HMDA), which can react easily at their chain ends, are deposited alternatively onto a substrate. The mechanism of the AVDP is schematically shown in Figure 1. It is necessary to prepare an activated sublayer with the amino end groups on the substrate surface (Figure 1 (a)) before the AVDP process. And each reaction cycle of the AVDP consists of a two-step procedure. In the first step, the evaporated ADC monomer is introduced to the system. The molecule may adsorb randomly and travel on the substrate surface. At the stage of molecular deposition onto the substrate, molecular orientation is strongly dependent on the substrate temperature^{8,12}. When the substrate temperature is kept sufficiently high, most molecules tend to the normal orientation. The probability of reaction at the both chain ends simultaneously on the substrate surface may be negligible. When one of the chain ends reacts on the substrate, the monomer molecule sticking with one of its chain end (hair molecule) on the substrate tends to form upright molecular orientation. Such upright molecules can not bend sharply to the substrate surface because of restriction of their bonding angle and conformational energy. Consequently, one of its chain ends can react with the amino groups on the surface with the elimination of HCl (Figure 1 (b)). The chemisorbed molecules exhibit higher molecular orientation perpendicular or tilting to the substrate. The by-product and the excess ADC monomer are evacuated from the system. The ADC monolayer is formed on the activated sublayer and its surface is covered with the chain ends of ADC (Figure 1 (c)). In the second step, HMDA is introduced to react with the chain ends of ADC to complete the first reaction cycle (Figure 1 (d)) and subsequently the excess diamine and HCl are removed from the system by vacuum-pumping. This

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results in the amido linkage (condensation reaction) yielding the activated surface covered with the amino groups that will be effective to initiate another reaction cycle (Figure 1 (e)), and so forth, until the desired number of bilayers are constructed. Accordingly, the repetition of alternating reaction can give rise to an increase in the molecular weight of the polymeric film without any chain folding because of the repetition of the monomolecular layer-by-layer epitaxial process.

In the present paper, nylon 66 films with a well defined structure are prepared by AVDP method and the conductivity of the films are studied as a function of temperature and humidity.

EXPERIMENTAL

Hexamethylene diamine (HMDA, $T_m=42^\circ\text{C}$) and adipoyl chloride (ADC, liquid state at room temperature and atmospheric pressure) were purchased from Tokyo Kasei Co. Ltd. and used without further purification. Each monomer can be easily vaporized at a relatively low temperature in a vacuum system without any change in the chemical structure. These two monomers can react easily at their chain ends at room temperature in the absence of any catalyst. Chromium and gold were deposited successively on a micro slide glass surface. Subsequently, the gold coated substrates were dipped in a 0.1% aqueous solution of 2-aminoethanethiol ($\text{HS}(\text{CH}_2)_2\text{NH}_2$, Tokyo Kasei Co., Ltd.) overnight at the ambient temperature in order to cover the substrate with the amino end groups which can react with carboxylic

Figure 1. Illustration of the mechanism of alternating vapor deposition polymerization of nylon system. (a): An activated sublayer on the substrate. Open triangles refer to the amino end groups. (b): ADC monomer reacts with the amino groups on the sublayer surface. Open circles refer to the chain ends of dichloride monomer. Solid circles and triangles are the reacted functional groups. (c): ADC monolayer covered with the chain ends of ADC. (d): HMDA monomer reacts with the chain ends of ADC. Open triangles refer to the diamine chain ends. (e): The first reaction cycle is completed to form an activated surface covered with the amino groups that can initiate another reaction cycle.

Figure 2. Schematic diagrams of circuit for electrical properties measurements along the film thickness direction (a) and along the direction parallel to the film surface (b) as well as Au comb-shaped electrodes and ADVP sample between the electrodes with a side view (c) and a top view (d).

groups in AVDP process. Preparation of AVDP nylon 66 film is the same in the previous studies¹³. The films were dried at 50°C under vacuum for overnight. As a reference sample, a conventional non-oriented nylon-66 film was prepared by an interfacial polymerization (IFP). IFP was carried out between 0.4 mol ADC in a carbon tetrachloride solution and 0.4 mol HMDA in an aqueous solution in the presence of 0.8 mol sodium hydroxide. IFP sample was cleaned with pure water and methanol and subsequently dried at 50°C for 6 hours in vacuum.

Transmission IR spectrum by a Micro Spectrophotometer (Jasco FTIR-100) and RAS IR spectrum by a Fourier transform IR system (Jasco FT-IR 7000) were recorded at room temperature in a dry nitrogen atmosphere. X-ray diffraction patterns were recorded by a conventional θ - 2θ diffractometer using Ni-filtered $\text{CuK}\alpha$ X-rays (Rigaku RAD-B) in the reflection mode. The film thickness was monitored in situ during AVDP process by a quartz crystal monitor (QCM) and the obtained film thickness was measured by an ellipsometer (EL-8, Optec Co., Ltd.) with an incident angle of 70° of the light from a He-Ne laser (632.8 nm).

In order to measure electrical conductivity along the film thickness direction, a gold top electrode was deposited on the film surfaces, whereas the gold substrate was served as a bottom electrode. An apparatus used in this experiment is schematically shown in Figure 2(a). Samples were placed in a cell in a dry nitrogen atmosphere or the ambient atmosphere of water vapor. Voltage was applied across the film by a power supply in the range of 0 to 5.2 volt D.C. Current through the film along the film thickness direction was measured with a

Figure 3. The relationship between the film thickness calculated from QCM and the number of reaction cycles (N) for AVDP films at a substrate temperature of 60°C.

Figure 4. The transmission and RAS IR spectra of AVDP film for $N=80$ at a substrate temperature of 70°C.

Figure 5. WAXD pattern of AVDP film for $N=20$ deposited onto the Au substrate at 60°C.

digital electrometer of Takeda Riken TR8652 type in the range of 50–200°C. Conductivity measurement of the film perpendicular to the film thickness was made by an electrical circuit shown in Figure 2(b). Comb-shaped Au electrodes were deposited onto the silicon wafers having a surface of SiO_2 insulating layer as shown in Figure 2(c) and 2(d). The wafers were treated by a β -(aminoethyl-aminopropyl-trimethoxy-silane) ($\text{H}_2\text{N}(\text{CH}_2)_2\text{-NH}(\text{CH}_2)_3\text{-Si}(\text{OCH}_3)_3$) as described previously¹³ in order to cover the substrate with amino end groups, which can react with the chain ends of ADC monomer during AVDP process. Thus, nylon 66 film can be formed on the substrate surface between the comb-shaped electrodes, depositing ADC and HMDA alternatively.

RESULTS AND DISCUSSION

Characterization of the film

Figure 3 shows the thickness for nylon 66-films prepared by AVDP as a function of the number of reaction cycles (i.e. the number of bilayers) monitored by a quartz crystal oscillator (QCM). The film thickness increases almost linearly with the number of alternating deposition reaction cycles (i.e. the degree of polymerization). The molecular weight of nylon-66 film was proportional to the film thickness¹³. This result clearly indicates that an increase in the film thickness is due to a chain-extending process from the substrate surface without chain folding. This was also confirmed by DSC data. DSC thermogram of AVDP film showed a single melting peak corresponding to the melting point of the nylon-66 crystal¹³. The melting temperature showed a linear relationship with the reciprocal of the degree of polymerization, indicating the melting behavior of the extended chain crystal.

Figure 4 shows transmission and RAS IR spectra for the film prepared at a substrate temperature of 70°C by AVDP. The film shows characteristic amide peaks at 3310 cm^{-1} (N-H stretching vibration), 1638 cm^{-1} (C=O stretching vibration) and 1543 cm^{-1} (N-H bending vibration). No peaks for residual monomers are found. These characteristic amide peaks increased linearly with an increase in the reaction cycle. The peak at 1638 cm^{-1} due to C=O stretching vibration having a transition moment perpendicular to the molecular chain axis appeared strongly in a transmission spectrum but weakly in a RAS spectrum. On the other hand, the peak at 1543 cm^{-1} due to N-H bending vibration having a transition moment parallel to the molecular chain axis appeared to be in a contrary result. The intensity ratio of the peaks at 1638 cm^{-1} and at 1543 cm^{-1} in the IR transmission spectra as a function of the number of reaction cycle showed almost constant¹³. This indicates that the molecular orientation in the film does not change during the layer-by-layer polycondensation by AVDP method.

Wide angle X-ray diffraction (WAXD) pattern of the film showed four sharp diffraction peaks associated with the reflections of the layered structure from first order to fourth order as shown in Figure 5. The first order peak was found at a diffraction angle of about 8.7° , corresponding to a spacing of 1.01 nm. The spacing is shorter than that calculated from the fully extended chain (1.72 nm)¹⁴ but roughly corresponds to the bilayer thickness estimated by QCM (1.21 nm) and by ellipsometry (1.31

Figure 6. The conductivity of AVDP films along the film thickness direction as a function of the film thickness measured at 90°C.

Figure 7. The relationship between the breakdown voltage at 90°C and the film thickness for AVDP films.

Figure 8. The effect of temperature on the conductivity for (○) AVDP film (prepared at 60°C with $N=80$) measured along the film thickness direction; (△) AVDP film measured in the direction parallel to the film surface; (□) IFP film casting from 1% trifluoroethanol solution measured along the film thickness direction.

nm). These results suggest that the molecular chains in the AVDP film are tilted at about 54° to the substrate normal. The inclination of the molecules could be associated with the hydrogen bonding between the amide groups of the adjacent molecules. The directions of hydrogen-bonding could be perpendicular to the film thickness direction. The film surface showed very flat in the order of optical microscopic scale and the domain structure was found in the transmission electron micrograph by the surface replica method. The surface of the domain was very flat and its size was about 0.3 μm . The film morphology will be reported in detail elsewhere¹⁵. These results indicate that a uniform nylon-66 thin film with well-defined structure is formed by AVDP.

Electric Properties of the film

Figure 6 shows an electrical conductivity along the film thickness direction as a function of the film thickness. The electrical conductivity shows an almost constant value of 2.5 pS/cm despite of an increase in the film thickness. This conductivity is good in agreement with reference data¹⁶. This indicates that the film consists of a uniform structure and the electrical conductivity is unchanged by the film thickness. A relationship between the breakdown voltage and the film thickness is shown in Figure 7. It reveals that the breakdown voltage decreases with increasing film thickness. The breakdown behavior is commonly observed in many polymer thin films¹⁷.

Figure 8 shows a typical reproducible curve for conductivity measured along the film thickness direction and perpendicular to the film thickness for AVDP film prepared at 60°C with $N=80$ and IFP film casting from trifluoroethanol solution. The conductivity for AVDP film shows anisotropic behavior over the whole temperature range. The conductivity of AVDP film perpendicular to the film thickness is larger than that along the film thickness direction. The conductivity along the film thickness direction of AVDP film is the least and one along the film thickness direction of IFP cast film is the greatest. The conductivity of IFP film is larger than that of AVDP films suggesting that different kinds and amount of impurities are contained in films. IFP films contain a trace of casting solvent, sodium hydroxide and by-product of sodium chloride. AVDP films contain un-reacted chain ends of amino and acid chloride groups at the polymer chain ends. Therefore, carriers could be sodium, chloride and proton ions in IFP films and chloride and proton ions in AVDP films. The hydrogen-bonding directions of AVDP film are almost perpendicular to the film thickness. The path of charge carriers along the hydrogen-bonding could be more effective than those along the molecular chain axis^{3,7}.

Figures 9 and 10 show electrical conductivity as a function of temperature and water vapor pressure along the film thickness direction for AVDP and IFP films, respectively. In Figures, one can divide three temperature regions, I: temperatures below the glass transition temperature T_g (ca. 70°C), II: temperature range from T_g to 100°C and III: temperatures above 100°C. In the regions of II and III, a straight line can be drawn. The conductivity is strongly dependent on water vapor below 100°C and very slight effects are found above 100°C. This observation makes no claim as to the nature of the

Figure 9. The effect of temperature on the conductivity along the film thickness direction for AVDP film (prepared at 60°C with $N=80$) under different water vapor pressures (P_{H_2O}). □ : 0 mmHg, ● : 17.5 mmHg, △ : 23.7 mmHg, ■ : 31.8 mmHg, ○ : 42.2 mmHg.

Figure 10. The effect of temperature on the conductivity along the film thickness direction for IFP film (casting from 1% trifluoroethanol solution) under different water vapor pressures (P_{H_2O}). □ : 0 mmHg, ● : 17.5 mmHg, △ : 23.7 mmHg, ■ : 31.8 mmHg, ○ : 42.2 mmHg.

Figure 11. The values of ΔE calculated from slopes in Figures 9 and 10 over the temperature range of 70–100°C as a function of water vapor pressures. ○ : IFP film, ● : AVDP film

water adsorption or the amount of adsorbed water in the film at each temperature.

Similar temperature dependencies have been found by Miyaji et al.⁶ They found three temperature ranges on temperature dependence of the conductivity of nylon-66: ① below 97°C, ② 97–250°C, ③ above 250°C. Below 97°C, the conductivity followed the *W.L.F.* equation and related to the chain rotation. Above 97°C, they proposed the ionic conductivity based on impurity ions but not amide protons and the conductive region in amorphous phase. The melting temperature of nylon-66 shows at about 245°C, indicating the other conductive behavior above its temperature. The temperature dependence of the conductivity showed also a distinctive change at T_g . Saito et al.⁵ adopted an ionic conduction based on a pressure dependence of the conductivity at 22–115°C and proposed a proton transfer through a hydrogen bonded network. They also found that the temperature dependence of the conductivity showed two straight lines broken at T_g in the direction parallel to the hydrogen bond but a single straight line in the direction perpendicular to the hydrogen bond. According to these experimental data, it could be concluded that the ionic conduction takes place in hydrogen-bonded polymers in the wide range of temperature. Small differences are found in the cross over temperature in the conductivity-temperature relationship between the data in this work and the reference data¹⁻⁶. These differences could be associated with the difference in film thickness and film structure. The film thickness in this work is about 0.1 μ m which is much thinner than that in the reference (about 10–100 μ m).

The electrical conductivity (σ) is expressed by the following Arrhenius equation^{3,4}

$$\sigma = \sigma_0 \exp\{-\Delta E/RT\} \quad (1)$$

where σ_0 is a constant, ΔE is the Arrhenius activation energy, R is the gas constant and T is the absolute temperature. According to slopes of the lines in the regions of II and III in Figures 9 and 10, the activation energy of conductivity is plotted against water vapor pressure as shown in Figure 11. The activation energy decreases with water vapor pressure and its decrement of AVDP film is larger than that of IFP film. A high dielectric constant of water leads to a reduction in the energy required for creating the charge carriers. The activation energy of the creation decreases with an increase in the dielectric constant. The activation energy in equation (1) can be rewritten by taking account of ionic dissociation as follows¹⁸,

$$\Delta E = (\Delta Q + \Delta w/2 \epsilon_1) + (\Delta w/2)(1/\epsilon_2 - 1/\epsilon_1) v_2 \quad (2)$$

where ΔQ is the activation energy for migration of ionic carriers, Δw is the ionic dissociation energy, ϵ_1 and ϵ_2 are the dielectric constant of polymer sample and water and v_2 is the volume fraction of water absorbed in polymer sample. The moisture content in nylon-66 increases linearly with the relative humidity¹⁹. In this study, v_2 is simply assumed to be a linear function to an ambient moisture vapor pressure with a proportional constant of C , such as $v_2 = C \cdot P_{H_2O}$. We also assumed the values for ϵ_1 and ϵ_2 to be 3.5 and 80, respectively.

Figure 12. The current density-electrical field characteristics of the AVDP films measured along the film thickness direction at 90°C with four different film thickness ($\circ$: $N=20$, $\square$: $N=40$, $\triangle$: $N=60$, $\diamond$: $N=80$). The solid line is obtained by fitting data based on equation (3).

Therefore, $C \cdot \Delta w$ and ΔQ are estimated from the slope and the line extrapolating to $v_z = 0$ in Figure 11, respectively. The values, thus obtained, are $\Delta Q = 23.4$ kcal/mol for IFP film and 23.2 kcal/mol for AVDP film. The activation energies obtained here fall within the reported values of 20–45 kcal/mol²⁰. Here, carriers ions are supposed to be impurities based on HCl for AVDP film and those based on NaCl for IFP film. Ionic dissociation energies for HCl and NaCl are 40 kcal/mol and 92.4 kcal/mol, respectively²¹. Based on these values, one can estimate the value C for AVDP and IFP films, yielding 0.071 and 0.013, respectively. These values are in good agreement with the reported data¹⁹. This suggests that water is absorbed in ADVP film more easily than that in IFP film. This result is consisted with the film morphology and structure. In fact, the surface of AVDP is covered with the chain end of amino and chloride acid groups and with the higher molecular orientation. The AVDP film surface can easily adsorb water vapor. On the other hand, there are no molecular orientation and no special surface structure in IFP film.

Figure 12 shows the current density – electric field characteristics along the film thickness direction at a measurement temperature of 90°C for AVDP films with four different film thickness. For all J – E measurements, the current density increases with increasing applied voltage. In particular, the J – E curves for all of the films obey the ohmic law at lower voltages then deviate from the linear response at higher voltages and finally display the breakdown behavior. At higher electric fields ($eEa \gg kT$) the current density J can be considered to be related to the applied field E by the approximation of hopping model²²

$$J = A \sinh(eaE / 2RT) \quad (3)$$

where e is the electronic charge, a is the hopping distance of the charge carrier, and A is a constant. In Figure 12, it is found that the experimental results are in good agreement with the formula described above, yielding the hopping distance of 3.5 nm at 90°C. This value coincides well with 4–5 nm²² obtained in most polymeric materials

CONCLUSION

The alternating vapor deposition polymerization (AVDP) was a useful method to produce a nylon 66 thin film with a higher molecular orientation perpendicular to the substrate surface. AVDP films had highly ordered structures with the molecular orientation normal to the substrate with the tilting angle of about 54°. The electrical conductivity of AVDP film along the film thickness direction showed almost constant (2.5 pS/cm) conductivity for AVDP film was anisotropic over the temperature range of 50–200°C. The conductivity in the direction parallel to the film surface was larger than that along the film thickness direction. Temperature dependence of the conductivity showed three temperature ranges: ① below T_g , ② $T_g \sim 100^\circ\text{C}$, ③ above 100°C. The electrical conductivity was strongly dependent on the water vapor pressure in the range of $T_g \sim 100^\circ\text{C}$ but was weakly affected by the water vapor above 100°C. The activation energy for the conductivity decreased with humidity in the range of $T_g \sim 100^\circ\text{C}$ but was almost constant (23 kcal/mol) above 100°C. Carriers were supposed to be impurities, such as a hydrochloric acid in AVDP films and sodium chloride in IFP films. Water vapor was adsorbed more easily in ADVP film than in IFP film. The ionic jump distance was estimated to be about 3.5 nm above T_g .

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