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Layer-by-layer polycondensation of nylon 66 by alternating vapour deposition polymerization

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Nylon 66 thin films were prepared by layer-by-layer polycondensation. Two kinds of bifunctional monomers were deposited alternatively onto the substrate. The films showed the highly ordered structure with the molecular orientation normal to the substrate. It was found that the thickness and the molecular weight of the nylon 66 film could be effectively controlled by the number of deposition reaction cycle. The molecular weight of the film was proportional to the film thickness. Copyright © 1996 Elsevier Science Ltd.

(Keywords: nylon 66; thin film; layer-by-layer)

INTRODUCTION

In recent years, many techniques, such as the Langmuir–Blodgett method, the chemical vapour deposition method and the vapour deposition polymerization (VDP) method, have been developed for fabricating polymeric thin films. Of these methods, the VDP method[1–4], is a powerful tool for producing polymeric thin films with a desired molecular orientation. For example, nylon 1010 films having normal molecular orientation on a substrate are obtained by the VDP method[1]. In the VDP process, two kinds of bifunctional monomers, such as a dichloride monomer and a diamine monomer, which can react easily at their chain ends, are deposited simultaneously or alternatively onto a substrate. It is necessary to prepare an active sub-layer surface, such as a substrate covered with amino groups as a surface active agent, prior to the alternating VDP (AVDP) process. A dichloride monomer is deposited onto the amino covered surface of the substrate, kept at an appropriate temperature at which the physisorption of the monomer molecules can be neglected. The arriving dichloride monomers can easily react with the amino groups on the substrate (chemisorption). This chemisorbed molecule can exhibit the normal molecular orientation[5] and its surface is covered with the chain ends of the dichloride monomer. That is, we can get the monomolecular layer of the dichloride monomer with the normal molecular orientation based on a self-organized-molecular deposition behaviour. Next, a diamine monomer is deposited onto the monomolecular layer of the dichloride monomer. The resultant film surface is covered with the chain ends of the diamine monomer, based on a similar mechanism to the former dichloride monomer layer. Thus the alternating reactions of two bifunctional monomers yield a polymeric film with the normal molecular orientation.

If the alternating VDP proceeds ideally, the film thickness is equal to the fully extended chain length (proportional to the molecular weight). It is possible to get an ultra-high molecular weight polymer in a polycondensation system. The present paper deals with the basic idea of the alternating layer-by-layer polycondensation to get an ultra-high molecular weight polymer.

EXPERIMENTAL

Hexamethylene diamine (HMDA, $T_m = 42°C$) and adipyl 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. P-type silicon wafers with a (100) plane (Mitsubishi Materials Silicon Co.) were cleaned with acetone, ethanol and ultra filtered deionized water and then cleaned by boiling ethanol. Subsequently, the wafers were treated in nitric acid (61%) to yield hydrophilic surfaces exposed by free –OH groups. The treated wafers were dipped in a 0.1% aqueous solution of a silane coupling agent, γ-(aminoethyl) aminopropyltrimethoxy silane ($H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$) at room temperature. Thus, the molecules of the silane coupling agent were fixed to the substrate with covalent bonds. The surface of the substrate was covered with the amino end groups of the coupling agent, which could react with carboxylic groups or isocyanate groups.

Figure 1 shows the scheme of the experimental apparatus. Several band heaters were wrapped around

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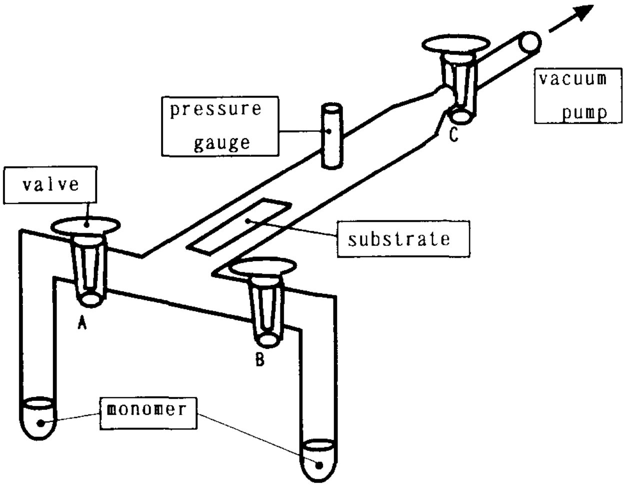

Figure 1 Scheme of the experimental apparatus for the AVDP process

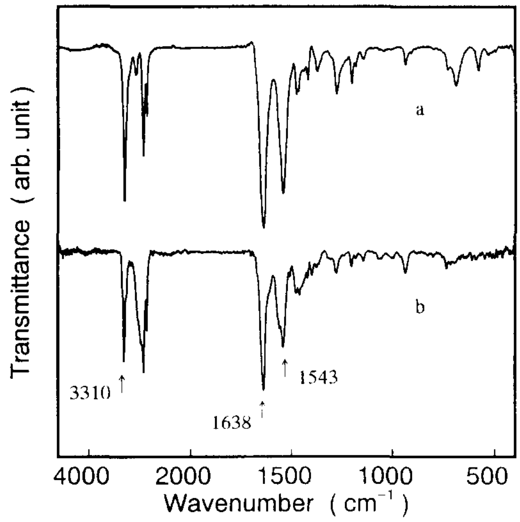

Figure 2 I.r. spectra for nylon 66 thin films prepared by interfacial polymerization (a) and alternating vapour deposition polymerization for 60 reaction cycles at a substrate temperature of 70°C (b)

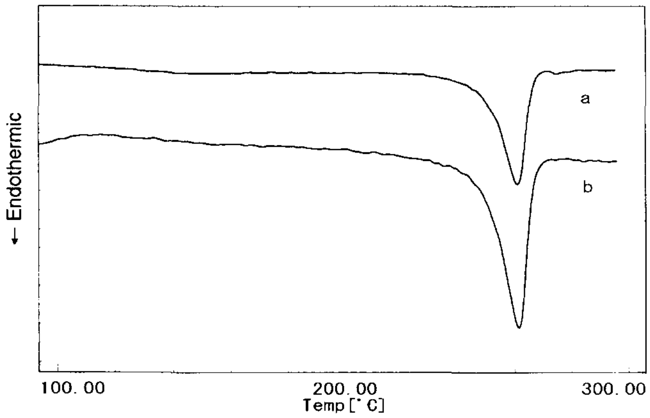

Figure 3 D.s.c. thermograms for AVDP sample at the substrate temperature ($T_s = 70°C$), the number of reaction cycles ($N = 40$) (a) and nylon 66 prepared by interfacial polymerization (b)

the apparatus to control the temperature of each individual section of the system. First, the system was evacuated to remove air by means of opening the valve C for a certain period of time, and ADC monomer was introduced into the system by opening valve A for 20 s. Next, valves A and B were both closed and valve C was opened to evacuate the residual monomers from the system for 5 min. Then, valve B was opened to introduce the vapour of HMDA monomer for 20 s. Valve C was opened again for 5 min after valves A and B were closed. This reaction cycle was repeated to get a desired film thickness.

Infra-red (i.r.) spectra were obtained with a transmission method using a Fourier transform i.r. (*FT*i.r.) system (Jasco FT-IR 7000) at room temperature in a dry nitrogen atmosphere. X-ray diffraction patterns were recorded using a conventional θ–2θ diffractometer using Ni-filtered CuKα X-rays (Rigaku RAD-B) in the reflection mode. The 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). The films on the substrate were scraped off from the substrates for determination of the molecular weight by viscometry in 90% formic acid at 25°C[6]. Differential scanning calorimetric (d.s.c.) measurements were carried out using a Shimadzu DSC-50 equipment in the nitrogen atmosphere at a heating rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

Figure 2 shows the transmission i.r. spectra for the film prepared by the alternating vapour deposition polymerization of ADC and HMDA at a substrate temperature of 70°C and for the film prepared by the conventional interfacial polymerization of nylon 66 as a reference polymer. The AVDP 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 the residual monomer were found. The films prepared by the AVDP method at the several other different substrate temperatures ranging from 60 to 100°C showed similar i.r. spectra to those obtained at a substrate temperature of 70°C. D.s.c. thermograms for AVDP film and the film prepared by the interfacial polymerization are shown in *Figure 3*. Both films show a single endothermic peak at 261°C, which corresponds to the melting point of the nylon 66 crystal. These observations indicate that nylon 66 thin film is formed directly onto the substrate without any residual monomers by the AVDP method.

Figure 4 shows the wide angle X-ray diffraction (WAXD) pattern of nylon 66 film prepared by the AVDP method. There are many sharp diffraction peaks which seem to be 001 reflections from the nylon crystals. This indicates the polymer chains can be orientated almost perpendicular to the substrate. The peak at a diffraction angle of about 8.7° corresponding to a spacing of 1.01 nm can be considered to the monomeric unit of nylon 66. Thus the diffraction peaks ranging from small to wide angle can be assigned, respectively, to (001), (002), (003) and (004), while their spacings are shorter than those calculated from the fully extended chain (1.72 nm)[7]. This may indicate that the polymer

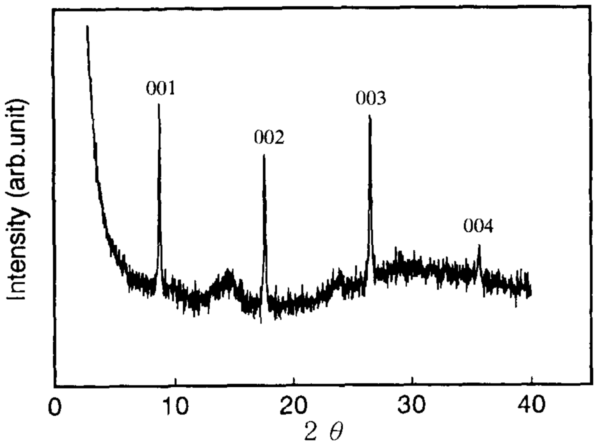

Figure 4 WAXD pattern of nylon 66 thin film deposited onto the substrate at 70°C and the number of reaction cycles ($N = 20$)

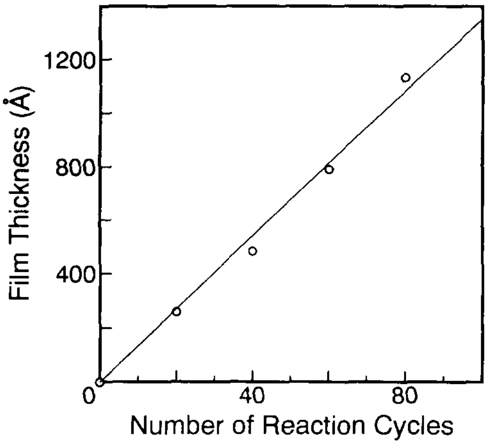

Figure 5 The thickness of nylon 66 films formed by the AVDP method at $T_s = 60°C$ as a function of the number of reaction cycles (N)

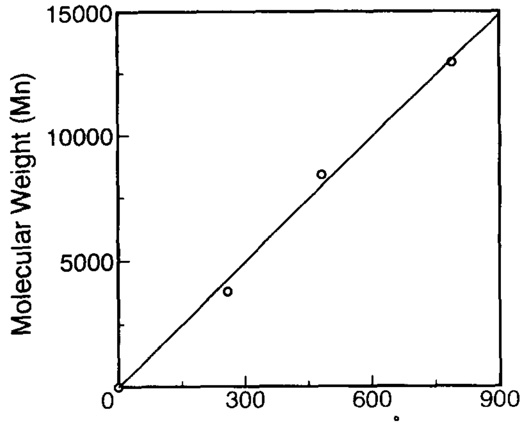

Figure 6 The relationship between the film thickness and molecular weight of nylon 66 film prepared by the AVDP method at $T_s = 60°C$

chains are tilted at about 54° to the substrate normal. No information for the lateral arrangement in the film was obtained since an X-ray diffraction pattern in $\theta - 2\theta$ geometry gives information only for the layer-by-layer arrangement in the film thickness direction.

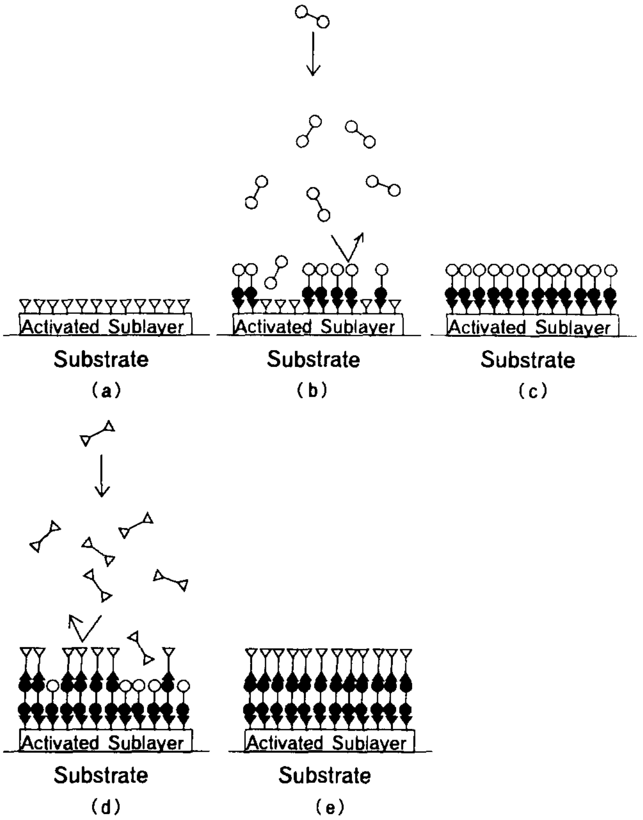

Figure 7 Illustration of the mechanism of alternating vapour deposition polymerization of nylon 66. (a) An activated sublayer on the substrate. Open triangles refer to the amino end groups of the silane coupling agent. (b) ADC monomer reacts with the amino groups on the sublayer surface. Open circles 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 5 shows the thicknesses of the films formed by AVDP as a function of the number of reaction cycles. It reveals that the thickness of the film increases linearly with the number of reaction cycles. In other words, the film thickness can be controlled by the number of reaction cycles. The layer thickness (1.31 nm) estimated from *Figure 5* roughly corresponds to the X-ray spacing of 1.01 nm discussed above. The relationship between the film thickness and molecular weight is illustrated in *Figure 6*. The molecular weight of nylon 66 film is proportional to the film thickness. This result clearly indicates that the increase in the thickness of the film is due to a chain-extending process from the substrate surface without a chain folding.

If the alternating vapour deposition polymerization can be performed ideally, a highly oriented nylon 66 thin film with a perfect layered structure can be constructed by the mechanism shown in *Figure 7*. Before the AVDP process, it is necessary to prepare an activated sublayer with the amino end groups on the substrate surface (*Figure 7a*). And each reaction cycle of alternating deposition polymerization consists of two-step procedures. In the first step, the evaporated ADC monomer is introduced to the system and its chain ends can easily react with the amino groups presented on the surface of the substrate with the elimination of HCl (*Figure 7b*). The by-product and the excess ADC monomers are evacuated from the system. Consequently, the ADC monolayer is formed on the activated sublayer and its surface is covered with the chain ends of ADC (*Figure 7c*). In the second step, the HMDA monomer is introduced to react with the chain ends of ADC to complete the first reaction cycle (*Figure 7d*) and simultaneously the excess diamine and HCl are removed from the reaction system under the vacuum system. This results in the amido linkages (condensation reaction) yielding the activated surface covered with the amino groups that will be valid to initiate another reaction cycle (*Figure 7e*), and so forth, until the desired number of monolayers are constructed. Such chemisorbed molecules can exhibit higher molecular orientation perpendicular to the substrate, since the monomer molecule sticking with one of its chain ends on the substrate tends to form normal orientation[8]. Therefore, it is remarkable that repetition of the alternating reaction, layer-by-layer, can given 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[5]. If the AVDP process is continued to hundreds of cycles, it will be possible to obtain an ultra-high molecular weight nylon 66. Furthermore, it is possible to get an ultra-high molecular weight condensation polymer, since the AVDP method can be applied to many other polycondensation systems.

CONCLUSION

The alternating vapour deposition polymerization is a useful method to produce nylon 66 thin film with a higher molecular orientation perpendicular to the substrate surface. The thickness and molecular weight of polymeric thin film can be effectively controlled by the number of reaction cycles during the alternating vapour deposition polymerization process. The AVDP method can be applied to prepare an ultra-high molecular weight polymer in a polycondensation system.

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