Formation of a thin film of poly(octadecyl methacrylate) using the physical vapour deposition technique

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Octadecyl methacrylate (ODMA) was deposited in the presence of red-hot wolfram filament. It was found that radical-initiated polymerization of ODMA occurred during its deposition. The polymer yield increased in conditions of high filament temperature, low deposition rate and high substrate temperature. Low deposition rate and high temperature (up to 280 K) affected the orientation of the deposited film. A low degree of supersaturation led to high polymer yields and improved orientation. The annealed deposited film has a structure like that of a Langmuir–Blodgett film.

(Keywords: physical vapour deposition; poly(octadecyl methacrylate); orientation; radical-induced polymerization; thin film)

INTRODUCTION

Preparation of polymer film by deposition has been known for many years[1]. Electrical discharge[2] or low energy bombardment[3] was used for initiating polymerization. In recent years, thin films of organic molecules have been used in electronic and optical devices. Langmuir–Blodgett (LB) and physical vapour deposition (PVD) techniques are well-known for the preparation of oriented thin films. Thus, LB film prepared from a monomer was polymerized to produce a stable, oriented film[4–9]. The PVD technique produces only oriented film, but is of value for making oriented thin films for devices in a dry system. In such a system, linear molecules like fatty acids have been deposited[10].

Octadecyl methacrylate (ODMA) is a chain-like molecule. The LB film of poly(ODMA) was formed directly from its polymer[11] and by polymerization initiated by electron beam[12] and ultraviolet light[13,14] of the monomer LB film. No research into the PVD of this monomer however, was undertaken.

We found that polymerization of ODMA was induced by a red-hot wolfram filament fixed in a vacuum vessel during its deposition. In this paper, we try to explain the polymerization initiation and investigate the effects of filament temperature, deposition rate and substrate temperature on polymer yield, thickness and orientation.

EXPERIMENTAL

Instrument

Figure 1 shows a schematic diagram of the PVD instrument. The vacuum vessel is 650 mm in height and with an i.d. of 310 mm. The vacuum vessel is made of a bell jar and a drum. The upper bell jar can be moved to introduce the substrates and substance for deposition. In the vacuum vessel are fixed a temperature controller for substrates (Kobayashi Rikakikai Co. Ltd), thickness monitor (IC-6000, INFICON), a shutter (100 mm in diameter), a wolfram filament (60 mm long and 0.24 mm in diameter) and two parallel plates. The distance between the two plates is 215 mm. The two plates are used for heating an aluminium crucible (10 mm i.d. and 11.5 mm in height) and for adjusting the substrate temperature. Aluminium foil was used as a partition between the plates to shield the substrate from light and heat.

Materials

Octadecyl methacrylate was purchased from Tokyo Kasei Kogyo Co. Ltd. Glass slides (Micro slide glass, 0.9–1.2 mm thick, 76 mm long and 26 mm wide, Matsunami Glass Ind. Ltd) were used for the substrates. Silver-coated glass slides were prepared using the PVD instrument (VPC-260, Japan Vacuum Ind. Co. Ltd). The thickness of the silver layer on the glass slide was 100 nm.

Physical vapour deposition

An aluminium crucible containing 40 mg of ODMA was fixed on the hot plate. Almost all of ODMA in the crucible was evaporated to substrate by heating the hot

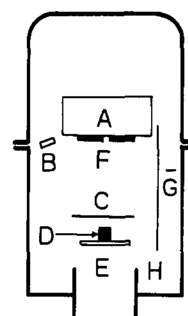

Figure 1 Schematic diagram of a physical vapour deposition instrument: A, temperature controller for substrates; B, thickness monitor; C, shutter; D, aluminium crucible; E, hot plate; F, substrates; G, wolfram filament; H, partition. The distance between substrate and hot plate is 215 mm

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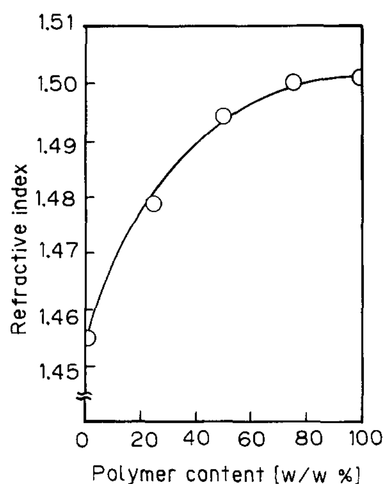

Figure 2 Relationship between refractive index and polymer content (w/w%) in the monomer

plate in a deposition experiment. The deposition rate was monitored by a thickness monitor maintained at 280 K. Various deposition rates were obtained by changing the temperature of the hot plate. Deposition was carried out at a pressure of 10^{-3} Pa.

Analytical methods

The temperature of the wolfram filament was estimated from its specific resistance.

The morphology of the thin film was observed with a differential interference microscope (Nikon Optiphoto, Nikon Co. Ltd).

Octadecyl methacrylate was deposited on silver-coated glass slides when the reflective infra-red (i.r.) absorption spectra of deposited ODMA were measured with an incidence angle of 10° (JIR-100, Japan Electronics Optics Laboratory).

The thickness of the thin films was measured with a nanoscope (Model 911-9150, Anerva) which applied multiple beam interferometry[15]. The step for measurement was made by scratching the centre of the film surface with a spatula.

The polymer yield was estimated from the refractive index of the thin film. *Figure 2* shows the relationship between the refractive index and the polymer content in the monomer. The polymer of ODMA was obtained by radiation-initiated polymerization. We assumed that the refractive index of the thin film was the same as that of a mixture of monomer and polymer when the polymer yield of the thin film was equal to the ratio of the mixture taken as reference. The refractive index of various mixtures of monomer and polymer were measured with an interference microscope (Reraval Interphako Interference Microscope, Carl Zeiss) using the same step for the thickness measurement. The refractive index of the thin film was calculated from the following:

$$n = \lambda R/Dt + n_0$$

where λ = wavelength, t = thickness, D = interval of interference fringes, R = shift of interference fringe, and n_0 = refractive index of control material. The reference substance for the thin film was air so that $n_0 = 1$.

X-ray diffraction patterns were measured with Cu Kα radiation.

The relative quantity of radicals produced during deposition was estimated using 1,1-diphenyl-2-picrylhydrazyl (DPPH) (Tokyo Kasei Kogyo Co. Ltd). A benzene solution of DPPH was evaporated onto the glass slides. The ODMA was evaporated towards the slide in conditions of no deposition at a temperature of 290 K for 40 min with a deposition rate of 1.2 nm min^{-1} in the presence of heated filament. The relative radical quantity was estimated from the decrease of absorbance at 536.6 nm (linear region).

RESULTS AND DISCUSSION

Influence of heated filament on deposition

Figure 3 shows a morphological change induced by heated filament in deposited ODMA. The ODMA was deposited as granular film without heated filament as shown in *Figure 3a*. The presence of heated filament changed this granular form to a film with uniform thickness which was transparent (*Figure 3b*).

We measured the polymer yield and the thickness of deposited film after deposition for various filament temperatures. *Figure 4* shows the effect of filament temperature on polymer yield and film thickness. Though no polymerization occurred without heated filament, the polymer yield increased with rise in filament temperature. Hence, we considered that polymerized ODMA film was formed by the deposition of ODMA monomer in the presence of heated filament. We assumed that the polymerization of ODMA caused the deposited film to have uniform thickness and be transparent. Otherwise the film thickness decreased slightly with rise in filament

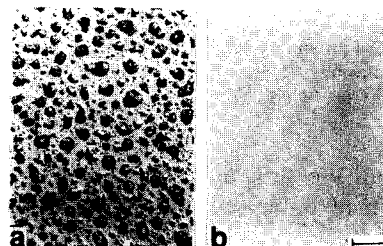

Figure 3 Photographs of deposited ODMA. Filament temperature: (a) 293 K; (b) 850 K. The ODMA was deposited with a deposition rate of 6.0 nm min^{-1} on substrate at a temperature of 280 K. Scale bar = 100 μm

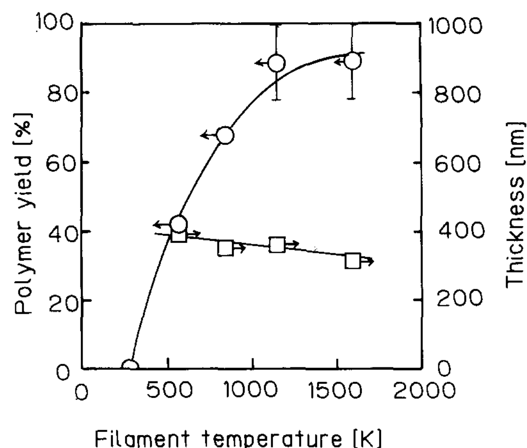

Figure 4 Effect of filament temperature on polymer yield (○) and film thickness (□). The ODMA was deposited with a deposition rate of 6.0 nm min^{-1} on substrate at 280 K

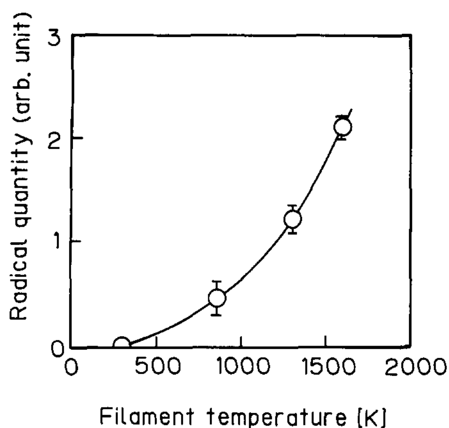

Figure 5 Relationship between the temperature of wolfram filament and the quantity of radical reaching the substrate

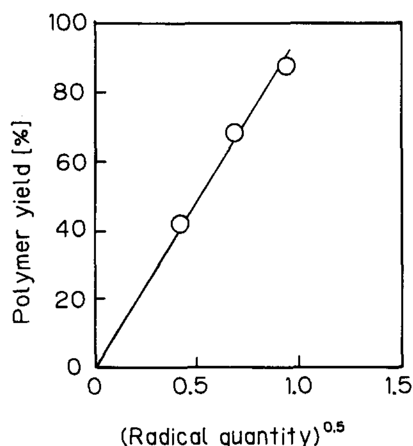

Figure 6 Plot of polymer yield *versus* (radical quantity)$^{0.5}$ for various filament temperatures. (Data of polymer yield and radical quantity were used for *Figures 4* and *5*)

temperature. We assumed that the active species for initiation of polymerization were produced by the presence of the heated filament. The active species appeared to reach the substrate and then react with the deposited ODMA. This is because the film of higher polymer yield would be thicker than that of lower polymerization yield if ODMA was mainly polymerized before reaching the substrate. The reacted monomers (like oligomers) rarely escape the substrate, while unreacted monomers on the substrate evaporate after a residence time.

Octadecyl methacrylate is a monomer which can polymerize in the solid state at a temperature <290 K by a radical mechanism[16,17]. We tried to measure the relative quantity of radicals which reached the substrate during the deposition of ODMA. *Figure 5* shows the relationship between the filament temperature and the relative quantity of radicals reaching the substrate during the deposition. It was confirmed that the relative quantity of radicals increased with rise in filament temperature. Therefore heating the filament caused radical production. Although the signal of the electron spin resonance spectrum of deposited film was too weak to identify these active species, we assumed that the radicals were decomposed ODMA fragments.

Charlesby reported that at low intensities the rate of radical-initiated polymerization is determined primarily by initiation rate, itself determined by radiation intensity I, and overall polymerization varies as I^n, with $n=0.5$ under steady-state radical conditions[18]. Hence, polymer yield for various filament temperatures is plotted against (relative quantity of radicals)$^{0.5}$ (estimated from *Figure 5*) in *Figure 6*. Radical-initiated polymerization occurring on deposited ODMA film was confirmed, since a linear relation was found between polymer yield and (relative quantity of radicals)$^{0.5}$. We concluded that the heated filament produces radicals which initiate the polymerization of ODMA deposited on the substrate.

Deposition rate

Figure 7 shows the effect of deposition rate on polymer yield and film thickness. The polymer yield was $\sim 15\%$ at a deposition rate of 24 and 54 nm min^{-1}. The polymer yield increased with decrease in deposition rate for a deposition rate <24 nm min^{-1}, while film thickness is reduced. The polymer yield reached 72% when the deposition rate was 1.2 nm min^{-1}.

The degree of orientation in the LB film of ODMA has been evaluated by i.r. spectroscopy[11]. We used i.r. spectroscopy to evaluate the orientation of deposited films. The coincident change of absorbance of both $\nu_{as}(CH_2)$ (2915 cm^{-1}) and $\nu_s(CH_2)$ (2848 cm^{-1}) in the reflective spectrum with low incident angle corresponds to the degree of normal arrangement of aliphatic chain in ODMA to the substrate, since the covariant transition moment of both $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ (2848 cm^{-1}) is situated in a plane perpendicular to the aliphatic chain axis[19,20]. Infra-red spectra of deposited films for various deposition rates were measured using an incident angle of 10°. *Figure 8* shows the effect of deposition rate on absorbance of 2915 and 2848 cm^{-1} normalized by the film thickness of 1.0 μm. The absorbance in the two absorption bands increased with decrease in deposition rate for a deposition rate <24 nm min^{-1}. This means that the normal arrangement of the aliphatic chain to the substrate is advantageous in the film prepared with the deposition rate <24 nm min^{-1}. Oriented film prepared with a low deposition rate has been reported using zinc stearate[21] and stearic acid[22].

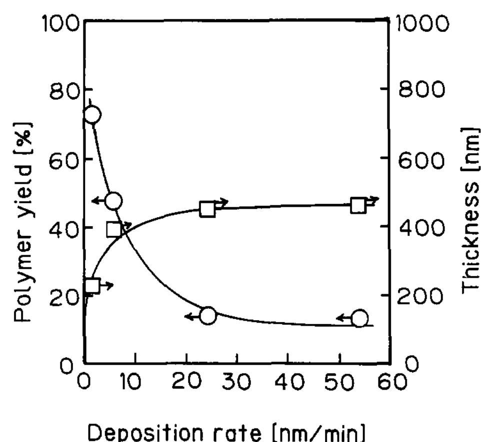

Figure 7 Effect of deposition rate on polymer yield (○) and thickness (□). Filament and substrate temperatures were 590 and 280 K, respectively

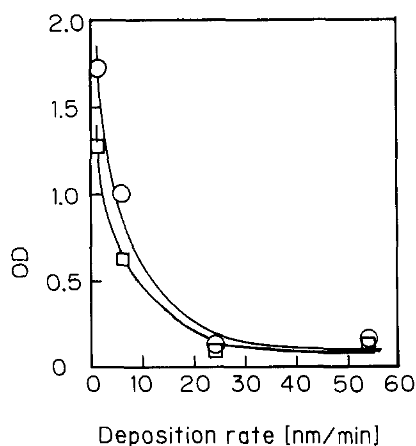

Figure 8 Absorbance for $\nu_{as}(CH_2)$ (2915 cm^{-1}, ○) and $\nu_s(CH_2)$ (2848 cm^{-1}, □) of deposited film for various deposition rates. Filament and substrate temperatures were 590 and 280 K, respectively

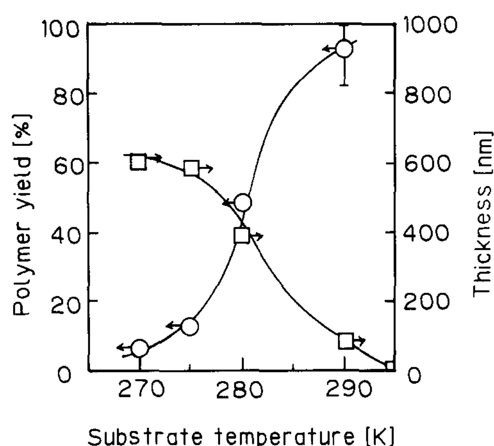

Figure 9 Effect of substrate temperature on polymer yield (○) and thickness (□). Filament temperature was 590 K and the deposition rate was 6.0 nm min^{-1}

Substrate temperature

Figure 9 shows the effect of substrate temperature on polymer yield and thickness. The thickness decreased with increase in substrate temperature >275 K. At a substrate temperature of 295 K, no ODMA was deposited on the substrate. The polymer yield increased with rise in substrate temperature.

Figure 10 shows the absorbance ($\nu_{as}(CH_2)$ 2915 cm^{-1} and $\nu_s(CH_2)$ 2848 cm^{-1}) of deposited ODMA film on the substrate at various temperatures. Both absorbances at 2915 and 2848 cm^{-1} increased with increase in substrate temperature up to 280 K. Correspondingly, the normal arrangement of aliphatic chains in the deposited ODMA increases up to 280 K.

Deposited molecules on the substrate undergo precession according to classical physics. At higher temperature the precession transforms to rotation and the normal arrangement to the substrate increases[23]. Inaoka *et al.* reported that increasing substrate temperature induced molecules to align normal to the substrate[22,24]. They explained that parallel molecules became unstable at high substrate temperature. The absorbance would have increased, if the phenomenon followed their explanation. However, absorbance decreased at a substrate temperature of 290 K. The polymer yield increased with increase in substrate temperature from 280 to 290 K, while the absorption at 2915 and 2848 cm^{-1} decreased in the same temperature range. We assumed that the polymerization increased in the disordered state. We assumed that polymerization occurred prior to the arrangement of the aliphatic chain of the deposited ODMA film at substrate temperatures >280 K, and that the arrangement of aliphatic chains was hindered by the polymer backbone[7].

We confirmed that controlling the deposition rate was more effective than controlling substrate temperature in order to obtain oriented ODMA film in the deposition of ODMA. This is illustrated by the absorbance in *Figure 8* changing from 0.11 to 1.72 with deposition rate and that in *Figure 10* changing from 0.37 to 1.02 with substrate temperature.

Degree of supersaturation

Matsuzaki *et al.*[10] proposed a concept of 'supersaturation' for the arrangement of deposited molecules. With a high degree of supersaturation, namely there are more incident molecules than escaping molecules, molecular chains are deposited in a random or horizontal arrangement with respect to the substrate. Otherwise, the molecular chains are deposited vertically on the substrate in the case of a low degree of supersaturation.

Hence, we tried to evaluate both polymer yield and degree of orientation based on the absorbance for $\nu_{as}(CH_2)$ (2915 cm^{-1}) from the viewpoint of degree of supersaturation.

The degree of supersaturation S is defined as follows:

$$S=(P-P_0)/P_0=(P-P_0/P)/[1-(P-P_0)/P]$$

where P is the actual vapour pressure during deposition and P_0 the equilibrium vapour pressure in the solid state. The term $(P-P_0)/P$ is equal to the adsorption rate/molecular flux rate during deposition. At a substrate temperature of 270 K for the ODMA deposition, we assumed

$$(P-P_0)/P=1$$

because $P \gg P_0$. Accordingly, this term is expressed as

$$(P-P_0)/P=L/L_{270}$$

where L is the thickness of the deposited ODMA film

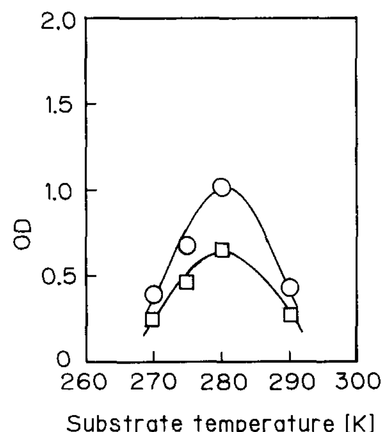

Figure 10 Absorbance for $\nu_{as}(CH_2)$ (2915 cm^{-1}, ○) and $\nu_s(CH_2)$ (2848 cm^{-1}, □) of deposited film for various deposition rates. Filament temperature was 590 K and the deposition rate was 6.0 nm min^{-1}

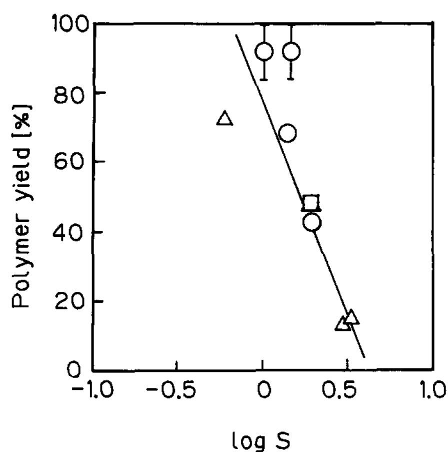

Figure 11 Relationship between polymer yield and logarithmic degree of supersaturation, *S*. Polymer yield for: various filament temperatures (○); various deposition rates (△); various substrate temperatures (□)

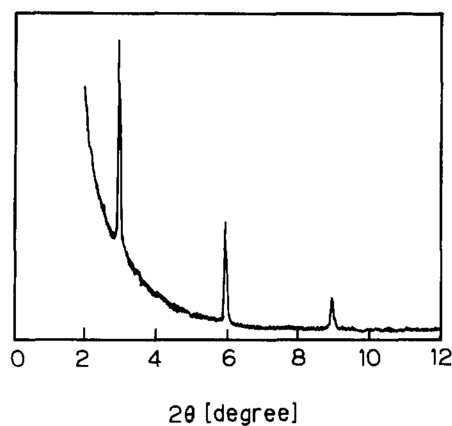

Figure 13 X-ray diffraction pattern of annealed ODMA film. The film was deposited in conditions of a filament temperature of 590 K, a deposition rate of 1.2 nm min^{-1} and substrate temperature of 280 K with annealing for 24 h at 293 K

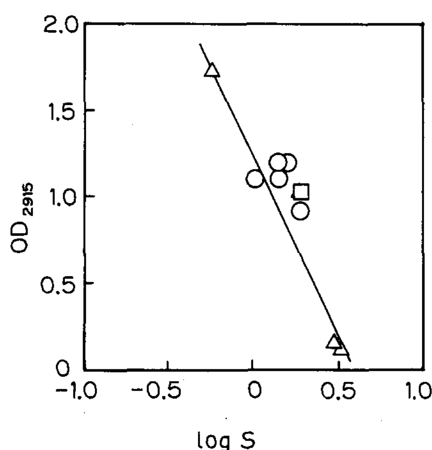

Figure 12 Relationship between absorbance for $\nu_{as}(CH_2)$ (2915 cm^{-1}) and logarithmic degree of supersaturation, *S*. Symbols as in *Figure 11*

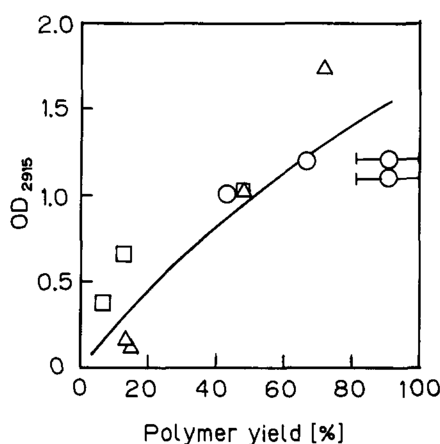

Figure 14 Relationship between polymer yield and absorbance of $\nu_{as}(CH_2)$ (2915 cm^{-1}). Symbols as in *Figure 11*

and L_{270} the thickness at a substrate temperature of 270 K. Therefore,

$$S = L/(L_{270} - L)$$

Figures 11 and *12* show the plots of polymer yield and absorbance for 2915 cm^{-1} for all filament temperatures, deposition rates and substrate temperatures (except 290 K) against the logarithm of degree of supersaturation. The polymer yield and the absorbance increased with decrease in degree of supersaturation. We assumed that the ODMA molecules had such a high mobility that they reacted quickly at the active sites of the ODMA polymer and aligned normally to the substrate, when the degree of supersaturation was low.

Annealing of deposited film

The deposition films had no X-ray diffraction pattern so they had no stacked structure as in LB films. However, the deposited films prepared with a deposition rate of 1.2 nm min^{-1} and substrate temperature 280 K were more oriented than the disordered films with preparation conditions of high deposition rate and low temperature (from i.r. spectra). We tried to obtain a film like an LB film by means of annealing, since *n*-hexatriaconate film was arranged perpendicular to the substrate by annealing[25]. Thus the deposited ODMA films were annealed at the glass transition point (293 K) of ODMA polymer.

Figure 13 shows the X-ray diffraction pattern of annealed ODMA film. This pattern appeared for a range of polymer yields from 42 to 72%. The film of polymer yield >80% had no X-ray diffraction after annealing. We suggest that the polymer backbone of ODMA hindered self-organization of the aliphatic chain[7]. In the case of polymer yield <17%, the uniform films converted to grain films. Nevertheless, no X-ray diffraction pattern was observed in the region ($2\theta = 3°$).

Figure 14 shows the relationship between polymer yield and absorbance of $\nu_{as}(CH_2)$ (2915 cm^{-1}) for ODMA deposition. The increase in both polymer yield and absorbance of 2915 cm^{-1} showed a correlation. This means that the films of polymer yield from 42 to 72% have higher orientation than those <17%. As a result, the degree of orientation appeared to be a factor in determining whether the deposited films changed to a stacked structure or not.

The layer space of annealed ODMA was 2.949 nm based on the diffraction pattern. Hatada *et al.*[12] reported an LB film of ODMA. In their study, the layer space of ODMA is 2.945 nm. We concluded that the X-ray diffraction of the deposited film was due to an arrangement of ODMA polymer in which the side chain

protruded on one side of the main chain in the deposited film.

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