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# ULTRA THIN ORGANIC AND POLYMER FILMS

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Preparation of ultra thin organic and polymer films could be divided into two methods. One is the wet process such as Langmuir-Blodgett (LB), spreading, dipping and casting methods. The other is dry processing, such as vapor deposition, sputtering, chemical vapor deposition, plasma polymerization and vapor deposition polymerization methods. Of these methods, the LB method has been attractive for the last decade to prepare a monolayer film, however, the vapor deposition method has also attracted attention for the preparation of well organized ultra thin films. It is important to investigate a molecular assembly in terms of the extent of aggregation, the crystalline regularity and their orientation in the thin film, since they are closely related to the physical, electrical and functional properties. This review focuses on an evaluation of the structure, molecular assembly and orientation in the thin films prepared by the LB and vapor deposition methods.

## Langmuire Blodgett (LB) Method

Kajiyama *et al.* (3208, 3211, 3214, 3234, 3237) have studied the morphology, crystalline defects content and viscoelastic properties for the LB films of long-chain fatty acids. The aggregation structure of monolayers composed of long-chain saturated fatty acids with different cohesive forces were investigated by transmission electron microscopy. The crystalline and amorphous states of the fatty acid monolayer depend on the relationship between the melting point of the monolayer and the temperature of the subphase. In addition, the crystalline defect structure of behenic acid monolayers was estimated by a single line method based on the Fourier analysis of the electron diffraction profiles. The crystalline lattice of the monolayer is not perfect even when the surface pressure is sufficient to

generate a surface morphology of the monolayer which is almost homogeneous. The crystallized monolayer from an amorphous state has a larger crystalline size and a smaller number of crystalline defects than the aggregated monolayer in the crystalline state. The relationship between the static viscoelasticity and the aggregation structure of the monolayer at the air-water interface was also studied. The temperature dependence of the maximum static elasticity is strongly related to the phase transitions of the monolayer or thermal monolayer motion of the amphiphilic molecules. The melting temperature of the monolayer is much lower than that of the bulk materials. The crystalline size ( $L$ ), the crystalline disorder ( $D$ ) parallel to the layer plane and the degree of crystalline distortion were also evaluated by X-ray measurement. The magnitude of  $D$  decreased with increasing length of the alkyl chains, indicating that an increase of the intermolecular aggregation force enhances the regularity parallel to the layer plane. The magnitude of  $D$  increased with increasing surface pressure, which may be due to the local collapse of the monolayer on the water surface owing to excessive compression. M. Sugi *et al.* (3225) reported that a model of flow orientation was developed for analysis of the in-plane anisotropy of the optical absorbance and the ESR line-shape observed in an LB film of a merocyanine and a fatty acid. The model refers to a two-dimensional fluid and a finite line-sink which represent the monolayer at the air-water interface and the substrate, respectively. The angular distribution function derived involves six parameters: the temperature  $T$ , the width of substrate  $a$ , the relative position on the substrate  $|x|/a$  and those involved in the Bingham-type rotatory friction coefficient  $\chi$  and the following equation was proposed:-

$$P(\tau) = \exp\{-(\chi G/kT)\sin 2\tau\}$$

where  $\tau$  is the angle between the long axis of an elongated particle and the dipping direction and  $G = (4/\pi) (V_d/a) (1-4X^2/a^2)^{-1}$ .

LB films of poly(p-phenylene-vinylene)(PPV) were investigated by Y. Imai *et al.* (3276) and S. Saito *et al.* (3279). Y. Imai *et al.* prepared the films in three steps: 1. Preparation of the monolayer film of the precursor poly(sulfonium salt) having perfluorononanoate counterion at air-water interface, 2. Deposition of the monolayer film of poly(sulfonium salt) onto an appropriate plate. 3. Thermal treatment of such multilayer film to form PPV films. The conductivity of the PPV film in the undoped state was about  $10^{-6}$  S/cm for the normal direction to the film and the conductivity of the  $\text{SO}_3$  doped film for the lateral direction was 0.5 S/cm. S. Saito *et al.* prepared the PPV film by the thermal elimination of sulfonium groups from the polyelectrolyte precursor films and obtained highly oriented PPV films, utilizing the formation of two-dimensional orientation of the PPV precursor with bilayer-forming amphiphile as counterion by the LB technique. Thus the LB films formed showed that the absorbance at the peak wavelength

(450nm) of a polarized light parallel to the dipping direction was about twice larger than that of the perpendicular one.

### Vapor Deposition Film

Vapor deposition is a useful method to obtain a thin film with molecular orientation perpendicular or parallel to a substrate. Such molecular orientation could be controlled by the deposition rate, a type of substrate and its temperature. Okui *et al.* (3742) have investigated the molecular orientation of the evaporated thin films of n-paraffines. The molecular orientation strongly depends on the deposition rate (i.e., supersaturation or molecular flux) and substrate temperature (i.e., supercooling which is defined by the difference between the melt temperature of the sample and substrate temperature). Small supercooling yielded the normal orientation and the high crystallinity in the film. Large supercooling brought the lateral orientation and the low crystallinity in the film. Small supercooling corresponds to a large degree of activity in the molecular motion on the substrate. In other words, the molecular orientation could be related to the molecular motion on the substrate, such as translation, rotation and precession. Of these motions, the precessional motions play an important role in the molecular orientation perpendicular to a substrate. K. Matshige *et al.* (3196) also studied the temperature dependence of the molecular orientation and its distribution for n-paraffin in the evaporated thin film by total reflection X-ray fluorescence microanalysis. The intensities of meridional reflections increase with temperature, that is, the normal orientation to a substrate increases rapidly with rise in temperature. On the other hand, the intensity of the 110 reflection decreases with temperature and disappears above 60°C. In the energy dispersive X-ray diffractometer, the orientational distribution can be also observed by changing the angle  $\alpha$  which is the angle between the incident X-ray beam and the surface of the substrate. Crystallites are normally oriented with a very narrow distribution around the normal orientation even in the as-deposited film and the population of crystallites with normal orientation is increased by heating without changing the shape of orientational distribution. The molecular orientation of 1,10-decanedicarboxylic acid was also studied by Okui *et al.* (1134). The deposition rate was found to increase discontinuously at the melting point of the dicarboxylic acid. Such deposition behaviour could be related to the presence of the hydrogen bond in dicarboxylic acid molecules. The molecular orientation of the film strongly depends on the deposition rate. When the dicarboxylic acid molecules were deposited onto a glass substrate kept thermostatically at 25°C, the lateral orientation was obtained at a deposition rate of above 5.5Å/s and the normal orientation was obtained at a rate of less than 1Å/s.

Hara *et al.* (1024) investigated thin films of nickel phthalocyanine by

organic molecular beam epitaxy growth (OMBE). The conductivity of the OMBE film was higher than that of the bulk sample and no doping effect using iodine was found. This fact can be attributed to good stacking in the molecular assembly which had never been obtained by conventional techniques. K. Kohda *et al.* (3148) reported on the fabrication and non-linear optical properties of highly oriented poly(diacetylene) thin films generated by the vapor deposition technique. The highly oriented poly(diacetylene) films was produced by means of the rubbing technique. The films obtained showed that the polarization ratio  $\alpha(\parallel)/\alpha(\perp)$  was as large ( $\sim 30$ ) and the third order susceptibility was about  $10^{-10}$  esu. Kato *et al.* (3193) also investigated the oriented poly(diacetylene) thin film prepared by solid-state polymerization. Long-alkyl diacetylene monomers were evaporated onto several substrates and subsequently solid-state polymerization was carried out by UV irradiation. The diacetylene monomer was oriented on the substrate kept at 25°C and poly(diacetylene) thin film polymerized from the oriented diacetylene film were found to be a single crystal in the region over a few  $\mu\text{m}^2$ .

Vapor deposition polymerization (VDP) has been employed for the preparation of thin films of polyamide aromatic polyimide and polyamide-imide. The process utilizes the coevaporation of two kinds of monomers with reactive functional groups at each chain ends, such as diamine and dicarboxylic acid. M. Iijima *et al.* (2972) investigated the preparation of thin films of aromatic polyureas from 4,4'-diaminodiphenylether or *n*-phenylene diamine and 4,4'-diphenylmethane diisocyanate by the VDP method. N. Okui *et al.* (1135) have investigated the oriented polyamide thin films obtained from 1,10-diaminodecane and terephthaloyl dichloride monomers by the VDP method. The polymer films obtained showed no peaks associated with the residual monomers in IR spectra, and many 001 reflections in the X-ray diffraction pattern. This indicates that the polymer film could be formed by polymerization of the monomers with a normal orientation to the substrate.