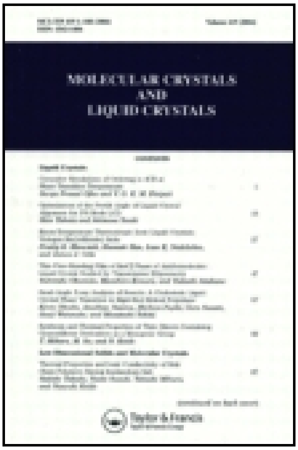

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PREPARATION AND CHARACTERIZATION OF LANGMUIR-BLODGETT FILMS OF POLY(p-(METHYL)PHENYL METHACRYLATES)

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Abstract The behavior of poly(p-(methyl)phenyl methacrylate) monolayer at the air-water interface was investigated. The surface pressure-area isotherms are dependent on a series of parameters such as molecular weight, temperature and compression-expansion cycle. The multilayer LB films are X- or Z-types and their pack ing and conformation are characterized by UV, FTIR and ellipsometry.

INTRODUCTION

The current state of art memory devices are being manufactured with feature size as small as 0.5-0.6 microns. The geometry size will decrease down to 0.3-0.4 microns in the next few years. I-line photolithography using conventional photoresists will be able to pattern the 0.3-0.4 micron structure, however, an alternative lithography will be required for the beyond of quarter-half micron. X-ray radiation, electron beam and scanning tunneling microscopy have been proposed as possible exposure systems for the next generation high resolution lithography.[1-3] In electron beam lithography the major limitation on the resolution is imposed by electron scattering, which causes a nonuniform incident exposure in the pattern structure. These resolution limits become more serious with increasing resist thickness. Therefore, the use of ultrathin resists with thickness below than 200nm has been proposed to improve the resolution limit of electron beam lithography.[4]

To prepare ultrathin polymer films on the surface of wafers, especially those of 8 inch diameter, uniformity becomes a serious factor in determining the quality of resist. The conventional spin coating method is no longer workable for preparing ultrathin polymer films on the large surface. The Langmuir-Blodgett(LB) technique has been proposed as being suited to the preparation of more uniform and defect-free ultrathin films with a controlled thickness to be made easily from a variety of organic materials.[5] There are already several papers studying on the fabrication of fine patterns on LB films, i.e., by Barraud[6] and others.[7-8] However, the sensitivity and thermal stability of resists prepared by LB technique using organic molecules are not sufficient to be used in the production line compared to those of spin-cast conventional polymer resists.

Recently lithographic results of fine patterns by positive resists using LB films of poly(methylmethacrylate)(PMMA)[9] and polyimide[10] has been reported. Thermally stable polyimide LB films are photosensitive to fabricate fine patterrns, but the limit of resolution of polyimide resist is not better than that of PMMA resist. PMMA resists are widely used in fabricating fine patterns by electron beam and x-ray lithography because of its best resolution capability in spite of their poor sensitivity. However, PMMA resists do not have thermal resistance to plasma etches typically used in advanced semiconductor device processing.

It is desirable to design a new radiation-sensitive polymeric imaging systems with improved sensitivity and resolution. In order to have the properties of polymer resists such as sensitivity, resolution and thermal stability, the model structure of PMMA was chosen to be modified. In general, the thermal stability of resist could be enhanced by introducing phenyl ring component to the resist structure. In the first attempt to test this concept, we prepared a number of PMMA derivatives containing methylphenyl ring unit in PMMA structure.

In order to establish a basis for understanding the lithographic performance of ultrathin polymer films, a better understanding of their structure at the molecular level is crucial. However, there has been very little effort in this area.[11] In the first approach to rationalizing polymer films at the molecular level, a study of thin-film behavior is required. An important feature of the thin films prepared by LB technique is the fact that the molecules may be present in the multilayers in an ordered structure, with very distinct orientational characteristics. It is very obvious that the characterization of the structure is a very important aspect of the study of monolayers at the air-water interface and of multilayers deposited on various substrates.

Anticipating better lithographic performance on designed resist of PMMA derivatives by electron beam, we first started studying the thin-film behavior of poly(p-(methyl)-phenyl methacrylate). The aim of the work presented in this paper is to examine the surface pressure-area characteristics of monolayer, depositon behavior and spectroscopic characteristics of multilayer films.

EXPERIMENTAL SECTIONS

Materials. α,α'-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol. Methacrylic acid, thionyl chloride, p-cresol, toluene, methanol were purchased from Aldrich and used without further purification.

Synthesis of Methacrylates. Poly(p-(methyl)phenyl methacrylates) were synthesized in three steps. Methacryloyl chloride was synthesized from methacrylic acid and thyonyl chloride. p-(Methyl)phenyl methacrylate (MPMA) was prepared by reacting methacryloyl chloride with p-cresol. The synthesis procedure of PMPMA was as follows. The mixture of MPMA(18.8 g, 0.11 mol) and AIBN(0.087 g, 0.5 mol %) in 44ml of toluene was refluxed under N_2 at 70°C for 48 hr. The product was precipitated with methanol and washed with methanol several times, and dried in vacuum.

Measurements. ^{1}H NMR spectra was recorded in $CDCl_3$ on a Bruker AM-300 spectrometer. IR spectra were recorded on an Shimazu IR-45 spectrometer and on a Nicolet 6000C FTIR spectrometers. A Harrick RMA-00G reflection attachment was used for RA measurements. The p-polarized infrared beam by a Hitachi wire-grid polarizer was incident on the plane at 85° from the surface normal. UV spectra were recorded on a Shimazu UV-256 spectrometer and also measured with a multichannel photodiode MCPD-1000 (Otsuka Electronics) through an optical fiber. Molecular weight determination was made by gel permeation chromatography (GPC) using Tosho HLC 2820 chromatograph. Contact angle measurements were done by Cahn Instruments DCA 322. Ellipsometric measurements were made with Rudorf EL ellipsometer.

Substrates and LB Film Preparation. Monolayer proprties were studied by using computer-controlled Lauda Filmbalance FW2. The surface pressure could be measured with an accuracy of about 0.05mN/m. The subphase was water, purified through a Milli-Q purification system attached with a reverse osmosis module. No significant surface pressure was measured before spreading of the polymer solution upon compressing the area to 2.5% of its initial value. PMPMA samples were spread from chloroform solution (0.5-1.0 mg/ml). Temperature and compression speed were varied. For the π-A isotherms the Langmuir film was compressed at the rate of 40 cm^2/min. For multilayer depositions the monolayer was compressed at the speed of 5 cm^2/min, and followed by an about 2 hr equilibrium period at the desired transfer pressure. The solid substrates of glass slides, quartz plates, silicon wafers(p-type, 100), ZnSe plate and silver coated glass slides were cleaned prior to use as described in elsewhere.[12,13] Hydrophobic substrates were prepared by treating in 5 mmol solution of dimethyldichlorosilane at the ambient temperature.

RESULTS AND DISCUSSION

Spectroscopic Assignments of Monomers in Bulk. Since assignment of monomer NMR spectrum provides a basis for interpretation of MPMA spectrum, the chemical shifts of the monomer were assigned in Figure 1. As interpretated in the MPMA structure in Figure 1, aromatic proton peaks appeared at 7.3–6.8 ppm. A doublet peaks at 5.7 and 6.4 ppm are characteristic of vinyl group. The protons at 2.3 ppm and 2.0 ppm are assigned to methyl

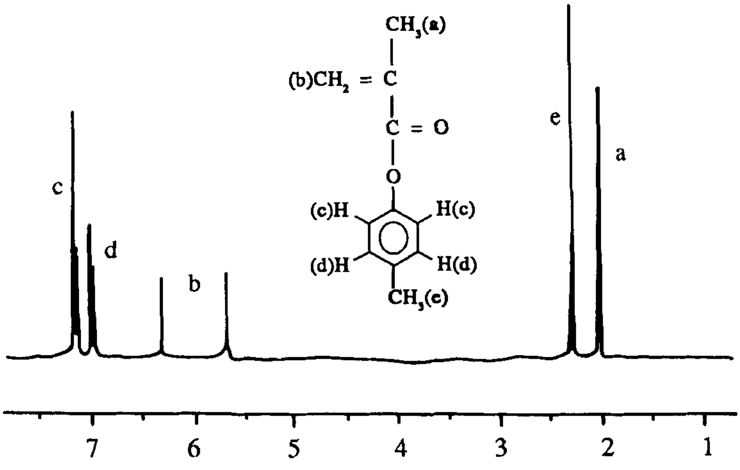

FIGURE 1. ^{1}H NMR spectrum (300 MHz) of MPMA in CDCl$_3$.

groups on aromatic ring and vinyl group, respectively. Figure 2 shows infrared spectra of monomer and polymer of MPMA, respectively. The C-H stretching bands at 3000-2850 cm^{-1}, C=O ester bands at 1730 cm^{-1} and C=C bands of alkene and aromatic ring at 1680-1475 cm^{-1} are very distinctive. The C=C alkene band of monomer at 1632 cm^{-1} completely disappears after polymerization as expected.

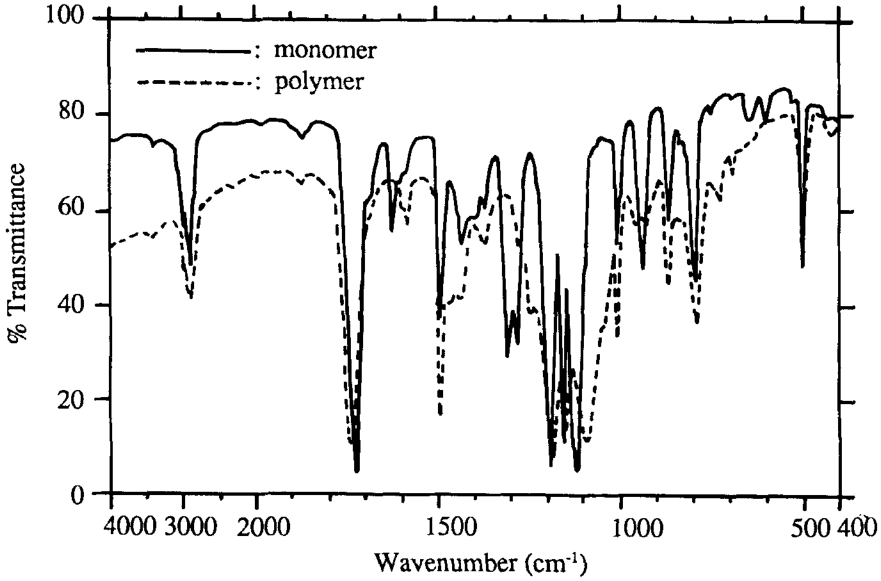

FIGURE 2. IR spectra of p-(methyl)phenyl methacrylate and poly (p-(methyl)phenyl methacrylate) on NaCl cell.

<u>Surface Pressure-Area Isotherms.</u> Figure 3 shows the surface pressure and area isotherms of PMPMA-1(M_w = 1.39 x 10^4) at the various number of compression cycles. Monolayer films of the expanded and condensed types can be distinguished based in part on the character of their π-A curves.[11] Expanded films were more compressible and exhibited reversible collapse. However, in the case of PMPMA-1 monolayer below a collapse surface pressure in the first compression the surface pressure at constant area falls precipitously. It is probably that several kinds of rearrangements may occur where the initial compression curve differs from subsequent compressions and expansions of the precompressed film. It is also observed that the compression and expansion curves are again identical below the collapse pressure if the monolayers are kept at the desired surface pressure for several hours. Figure 4 shows the isotherms of PMPMA-1 as a function of temperatures. It is clear that the area per repeating unit decreases as the temperature increases from 8 °C to 40°C, thus the surface pressure of the monolayer associated with a constant area per monomeric unit decreases with increasing temperature. This phenomenon is opposite to what would be expected for an entropy-associated pressure. The unexpected temperature dependence of the surface pressure of PMPMA-1 can be explained by temperature-dependent lateral cohesive interaction energies. The order required to align the ester groups of PMPMA to-

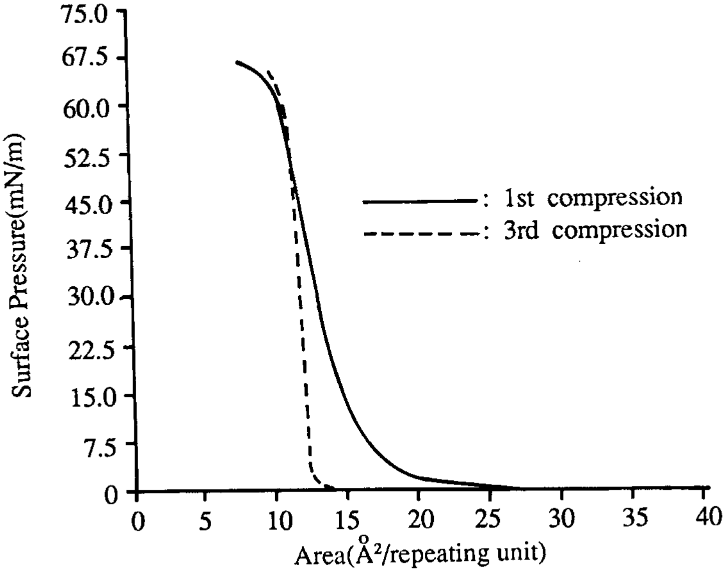

FIGURE 3. Compression-expansion cycling of PMPMA-1; compression speed 40 cm²/min, temperature 22.0 °C.

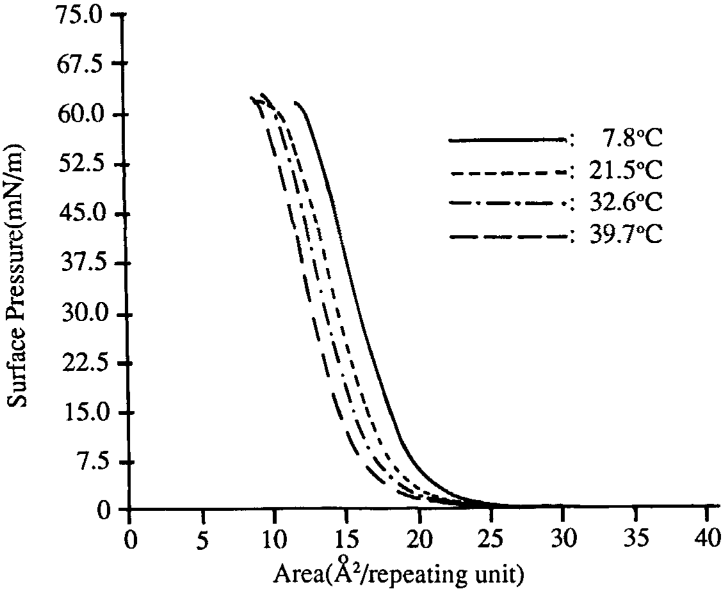

FIGURE 4. Pressure-area isotherms of PMPMA-1; compression speed 40 cm²/min.

ward the water phase could be disturbed by the thermal movements of the polymer chain segments as the temperature is raised. This result is similar to Schouten's results with the isotherms of isotactic PMMA as a function of temperature.[12]

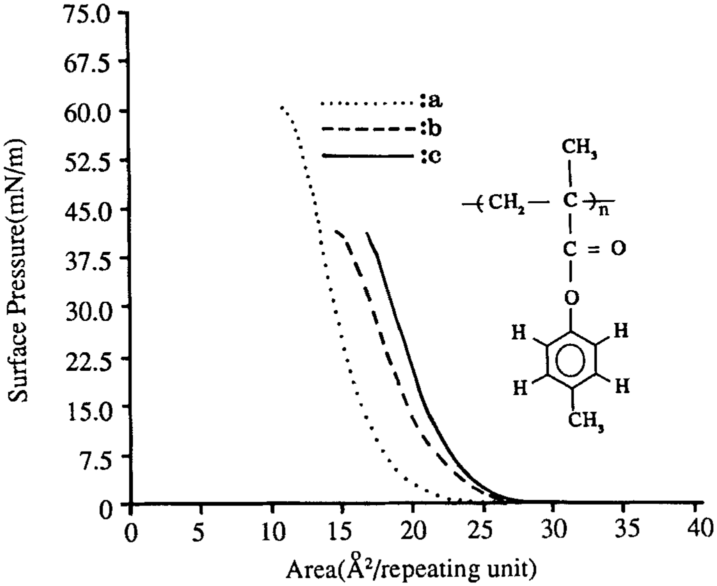

FIGURE 5. Pressure-area isotherms of PMPMA ; temperature 21.8°C, compression speed 40cm^2/min, concentration (a) 2.91 x 10^{-6}mol/L of PMPMA-1, (b) 5.76 x 10^{-6} mol/L of PMPMA-2, (c) 1.15x10^{-6} mol/L of PMPMA-2.

Figure 5 shows the isotherms of PMPMA-1 and PMPMA-2 as a function of concentration and molecular weight. As seen in Figure 5a and Figure 5b the isotherm of PMPMA-2 shifts to higher areas. It is also observed that the isotherm of the low-molecular-weight PMPMA series is shifted to relatively higher area compared to high-molecular-weight PMPMA series. Due to incomplete spreading of the high-molecular-weight PMPMA series the apparent area per repeating unit at the limit of zero surface pressure shifts from 23.4 $\mathring{A}^2$ (PMPMA-3, $M_w = 1.61 \times 10^4$, 5.67 x 10^{-6} mol/L) to 22.3 $\mathring{A}^2$ (PMPMA-2, 5.76 x 10^{-6} mol/L) at the similar concentration.

Uniformity of Monolayers. Information about the uniformity of polymer monolayer can be obtained from *in-situ* UV measurement of monolayer on a water surface. Figure 6 shows absorption spectra of PMPMA-1 monolayer on pure water at various surface pressures. The UV absorption measurements were taken from the same area of monolayer at the near pressure sensor. In the case of PMPMA ,which is a case of benzoyl derivative, the positions of primary and fine-structure bands can be calculated on the basis of empirical rules of benzoyl derivatives.[13] The two primary and one fine-structure bands of pure parent chromophore should appear at around 220, 240 and 280 nm, respectively. One major peak appeared at 230 nm and its intensity varied, depending on the surface pressure. This peak is assumed as a fine structure band that is shifted to the shorter wavelength region. On the basis of absorption spectra depending on the surface pressure it is probably that the surface pressure increases with increasing the packing density of PMPMA monolayers. However, once compared the absorption intensities of monolayers near the moving barrier with that

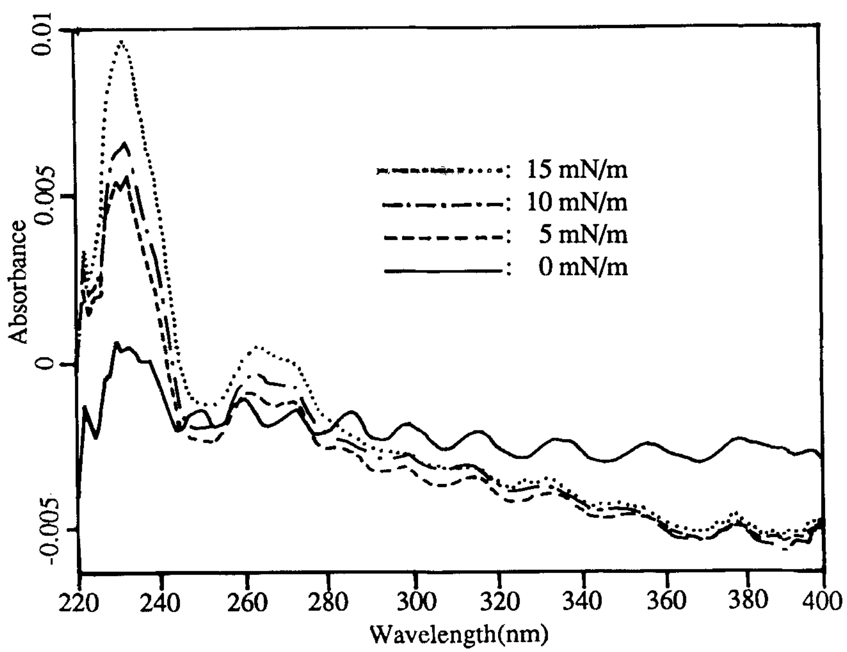

FIGURE 6. UV absorption spectra of PMPMA-2 monolayer on the water surface at various surface pressures ; compression speed 5 cm^2/min, temperature 23 °C.

of monolayers near the pressure sensor, a big absorption difference was observed. The absorption intensity near the moving barrier was bigger as much as 7 times than that near the pressure sensor. It is believed that the packing density of rigid PMPMA monolayers are not uniform on water surface.

Formation of Multilayer Films. The most common and thermodynamically stable multilayer structures are of the Y-type, where the layers are deposited in a head-to-head, tail-to-tail fashion. In certain cases, Z-type deposition could be obtained by decompression or removal of the monolayer from the air-water interface prior to down stroke. Several polymeric systems of genuine Z-type depositions have been previously reported.[17,18] The deposition behavior is determined by the shape of the water meniscus during deposition. Dimethyldichlorosilane treated cover glasses and silicon wafers are strongly hydrophobic, both advancing and receding contact angles are 90 °. In the case of PMPMA, deposition occurs only during the down stroke on hydrophobic substrates and only with upstroke on hydrophilic substrates. Figure 7 shows the transfer ratio in contrast with the numbers of vertical dipping on hydrophilic substrate at the different surface pressure. All Z-type depositions were observed with the transfer ratio below 0.6 at the relatively higher surface pressure. Hydrophobic substrates had better transfer ratios (ρ = 0.6 - 0.9) for X-type deposition only on down stroke dipping. Compared to the vertical deposition the horizontal dipping drove a better transfer ratios with PMPMA on the various substrates such as silicone wafers, glass slides, gold coated cover glasses and quartz plates. The best transfer ratio (ρ = 0.91) was obtained on gold coated cover glass at the surface pressure of 5mN/m.

Figure 8 shows UV spectra for different number of layers deposited on both sides of

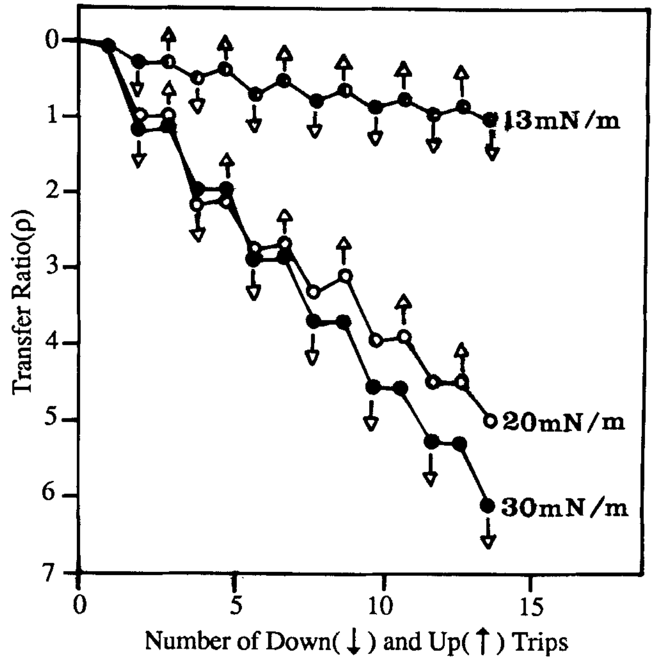

FIGURE 7. Effect of surface pressure on the transfer ratios for PMPMA-1; speed of up and down strokes 3mm/min, temperature 22.0 °C.

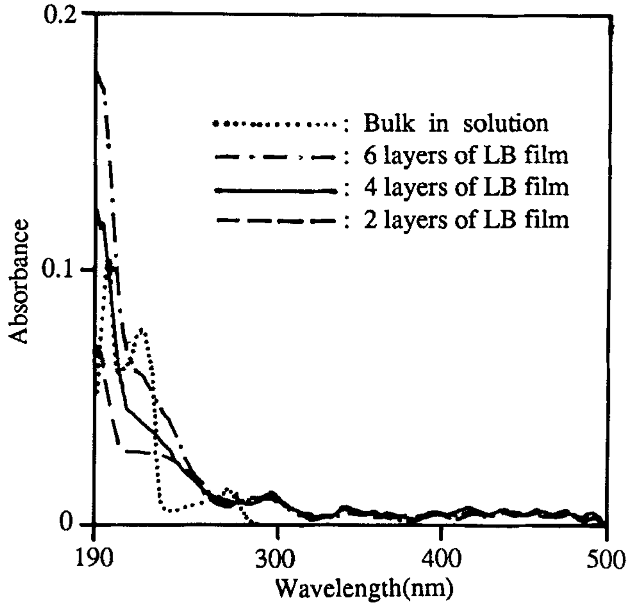

FIGURE 8. UV absorption spectra of PMPMA-2

quartz substrates and for a bulk in solution. As discussed in Figure 6, two major peaks at around 230 and 270 nm were observed in bulk in nonpolar cyclohexane solution. These peaks shift to the shorter wavelength region once multilayer LB films deposited on quartz substrates. It is not easy to assign the position of primary band in the short wavelength region below 200 nm. However, the intensity increasement is proportional to the number of layers deposited on quartz plates. This is an indirect evidence of layer growth of PMPMA on the substrates.

In order to evaluate the uniformity of PMPMA layers deposited on the solid substrates, the film thickness of various multilayers deposited on hydrophobic silicon wafers was measured. All samples were prepared by horizontal deposition instead of vertical depositon at the best dipping conditions for the best film quality. The ellipsometric measurements were carried out in air at one angle of incidence ($\theta = 70^\circ$). The thickness of each films were calculated automatically, using the refractive index of PMPMA for the layer (Nf = 1.46 - 0i) and substrate optical constants as measured from a blank sample (Ns = 3.432 - 0.08i). Ellipsometric results indicate that the average layer thickness per layer is 9 Å + 1 Å. The thickness of PMPMA layer could be higher than 10 Å because of the low coverage of PMPMA LB films on substrates. Further investigation on the determination of exact film thickness is necessary.

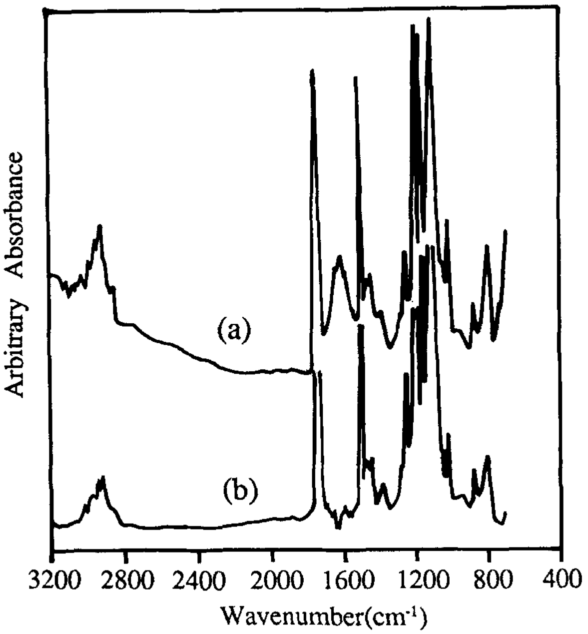

FIGURE 9. Infrared spectra of PMPMA-2 ; (a) transmission spectrum on a ZnSe plate, (b) reflection-absorption spectrum on an evaporated Ag film, p-polarizedradiation, angle of incidence 85°.

Figures 9 (a) and 9 (b) represent infrared transmission and RA specrta, respectively, of PMPMA-1 LB films. Compared to the transmission spectrum of PMPMA bulk in figure 2, most of bands are very similar except a prominent change at 1604 cm^{-1} region. The symmetric and antisymmetric stretching bands at 3100 - 2850 cm^{-1}, the antisymmetric COO^- stretching band at 1515 cm^{-1}, C=O band at 1730 cm^{-1} are characteristics of PMPMA. The in-plane vibration band of benzene ring at 1604 cm^{-1} are much weaker in the RA spectrum than in the transmission spectrum. Since the electric field of the infrared beam is parallel to the LB film in the normally incident transmission measurements, while perpendicular in the RA measurements, it is suggested that the molecular orientation of benzene plane in the PMPMA structure tend to orient parallel to the film surface.[19] The molecular conformation of PMPMA is rather different from the suggested conformation of poly(octadecyl) methacrylate at the air-water interface.[15]

CONCLUSIONS

It has been demonstrated that stable monolayer of PMPMA are formed on a water subphase and transferred to various solid substrates by means of vertical and horizontal dipping techniques. The monolayer uniformity of PMPMA on a water subphase is not same , depending on the location for UV measurements. It is believed that noncentrosymmetric multilayers, either X-type or Z-type, are formed on various substrates. The monolayer behavior of PMPMA is dependent on a series of parameters (molecular weight, temperature, compression speed, compression-expansion cycle), so that the characteristics of the monolayer can be easily varied.

The orientation of benzene plane in PMPMA LB films is most probably parallel to the film surface. UV and ellipsometry data suggest that the thickness of multilayers proportionally increases as the number of layers increases. The conformation and crystallinity of multilayer film is not clear yet, so that further spectroscopic investigations on multilayer films of PMPMA is required.

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