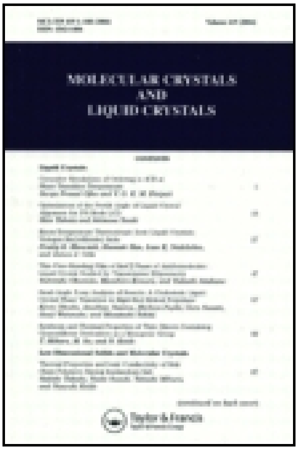

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Transfer Characteristics of Langmuir-Blodgett Films of Stereoregular Poly(Methyl Methacrylates)

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TRANSFER CHARACTERISTICS OF LANGMUIR-BLODGETT FILMS OF STEREOREGULAR POLY(METHYL METHACRYLATES)

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Abstract Systematic investigations of the effects of the transfer pressure, types of the substrates and stereoregularity on the transfer characteristics of the stereoregular PMMAs were performed in terms of the average transfer ratio. All of the stereoregular PMMA monolayers showed similar tendencies in transfer characteristics with respect to the transfer pressure. Z-type multilayers were formed at a transfer pressure below 1 mNm^{-1} for the *a*- and *s*-PMMAs and 5 mNm^{-1} for the *i*-PMMA, respectively. The average transfer ratio of the downward stroke increased as the transfer pressure increased from those values, forming Y-type multilayers at the transfer pressure of 10 mNm^{-1} for the *a*-PMMA and *s*-PMMAs and at 15 mNm^{-1} for the *i*-PMMA, respectively. The effect of the types of the substrate on the transfer characteristics was not significant except for the glass substrate when the first layers were baked.

INTRODUCTION

Poly(methyl methacrylate) (PMMA) Langmuir-Blodgett (LB) films have attracted significant interests recently because of their application potentials in nanolithography and nonlinear optics[1-3]. PMMA is known to give the highest resolution when used as an electron beam resist[1]. Along with the thinness of the LB films, PMMA LB films have been used as an electron beam resist to form nanometer scale patterns by electron beam lithography[1,2]. PMMA and its derivatives have also been actively studied as a waveguiding material because of their low optical loss[3,5]. PMMA has been tried as a host matrix with highly nonlinear optical guests in the guest/host nonlinear optical material systems[3,5]. Noncentrosymmetric structure is required for a material to have second order nonlinear optical properties. Formation of X- or Z-type LB films is important in this respect.

There are three types of PMMAs depending on the stereoregularity[6]: *isotactic* (*i*-), *syndiotactic* (*s*-) and *atactic* (*a*-) PMMAs. Although the different stereoregular PMMAs were found to result in significantly different surface pressure-area (π-A) isotherms about 30 years ago[7], it is only in recent years that details of the molecular information related to the differences in the π-A isotherms have been studied[8-10]. Different stereoregular PMMAs has been found to have distinctly different molecular arrangements at the air-water interface[8,10].

In general, formation of LB films is influenced by molecular arrangement and rigidity of floating monolayers, subphase conditions, types of substrates, dipping speed and flow patterns[13]. Since the molecular arrangement of the stereoregular PMMAs is different from each other, thus the transfer characteristics is expected to be. These can be found in the results reported previously. For instance, Kuan *et al.*[1] reported the formation of Y-type LB films of the *a*-PMMA on the Cr substrate at a transfer pressure of 10 mNm^{-1}. Stroeve *et al.*[3] reported the formation of Z-type LB films of the *s*-PMMA on the glass substrate at a transfer pressure of 12 mNm^{-1}. Brinkhuis and Schouten[8] reported the formation of Z- and Y-type LB films of the *i*-PMMA on the gold substrate at the transfer pressure of 5 and 12 mNm^{-1}, respectively. Different transfer characteristics reported earlier may come from the differences in the stereoregularity and the tranfer pressure or from the substrate they used. However, to our knowledge, there has been no attempts to investigate the transfer characteristics of PMMA LB films in terms of stereoregularity, transfer pressure, substrate characteristics, etc.

The centrosymmetric Y-type structures have good quality molecular assemblies, low pinhole density and hence are suitable when applied, for example, as resist in lithography. However, Z-type structures are required in the field of nonlinear optics, pyroelectricity and piezoelectricity[12] as mentioned previously. In view of the applications, it is important to obtain the desired structure by properly controlling transfer variables.

In this paper we report on the effects of the transfer pressure, types of the substrates and the stereoregularity on the transfer characteristics of PMMA LB films in terms of transfer ratio and the molecular arrangements of the floating monolayers.

EXPERIMENTAL

All of the stereoregular PMMAs were purchased from Polyscience Inc. and used

TABLE 1 Material characteristics of stereoregular PMMAs[13].

Tacticity	Mw	Mw/Mn	Contents of Triads(%)			Tg (deg C)
			I	H	S	
a-PMMA	185,000	1.05	15	37	48	100
s-PMMA	100,000	1.9	6	10	84	123
i-PMMA	250,000	4.3	97	2	1	51

I : isotacticity, H : heterotacticity, S : syndiotacticity

without further purifications. Their physical properties are listed in Table 1. The materials were dissolved in spectroscopic grade chloroform purchased from Fluka Chemie AG and were spread on deionized water with the resistivity of 18 MΩ-cm.

Measurements of the π-A isotherms, the surface potentials (ΔV), and the transfer of floating monolayers were performed using a constructed normal type Langmuir trough (length, 550 mm; width, 200 mm). The π-A isotherms were measured by the Wilhelmy plate method with a readibility of 0.025 mNm^{-1}. The Wilhelmy plate was located 10 cm apart from edges of the trough and a weight of 3 g was attached to the plate to prevent it from tilting during the monolayer compression. Surface potentials were measured by using vibrating plate method (KSV 5000 SP). The trough was placed in a clean room of class 1,000 maintained at 20 ± 1 ℃. Monolayers were compressed and released at a rate of 20 cm^2 min^{-1} 20 min after spreading to allow the solvent to evaporate. For the transfer, monolayers were compressed to the transfer pressure at the same rate, followed by about a 90 min stabilization period. Here, stabilization means the state at which there are no changes in monolayer area within a 10 min period while the surface pressure maintains within the deviation of 0.05 mNm^{-1}.

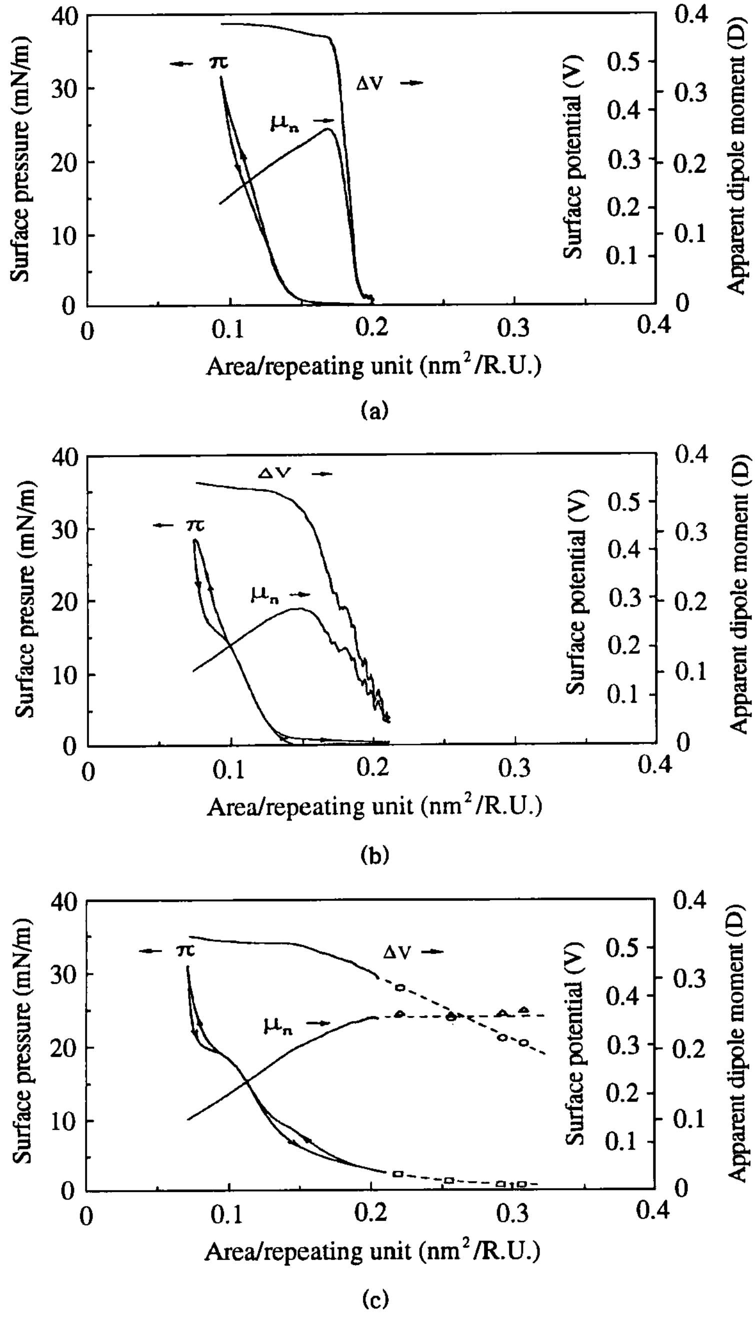
The floating monolayers were transferred onto a cover glass, Al, Cr, Au and Si substrates at the surface pressure of 1 - 20 mNm^{-1}. The cover glasses were cleaned by submerging them into a concentrated chromic acid-sulphuric acid solution for 30 min and then repeatedly rinsed with deionized water. The cover glasses were dried in a convection oven at 100 ℃ and then stored in wafer carrier. Al and Au substrates were prepared by thermally evaporating Al and Au metals of about 500Å on both sides of the silicon wafers. Electron beam evaporation was used for the preparation of the Cr substrates. Just prior to the transfer, all the substrates except Si substrates were subsequently rinsed with acetone, methanol and deionized water and then dried with filtred nitrogen. Si substrates were submerged into buffered oxide etchant solution for 1 min to remove the natural oxide and then rinsed with deionized water followed by drying with filtred nitrogen. Contact angles of the substrates that were measured by the sessile drop method[14] are 39.1, 39.7, 70 and 76.8 for the Cr, Al, Au and oxide etched Si substrates, respectively.

The transfers of monolayers were made by the vertical dipping method with dipping speed of 2 mm min^{-1}. The substrates were positioned 2 cm apart from the Wilhelmy plate. The first layers were always transferred during the upward stroke. In some cases, the first monolayers were baked at 100 ℃ in a convection oven for 10 min prior to the next downward stroke in order to prevent the peeling off during the successive transfer.

RESULTS

The π-A isotherms, the surface potentials and the apparent dipole moments (μ_n) of monolayers of *a*-, *s*- and *i*-PMMAs are shown in Fig. 1(a), (b), and (c), respectively. The π-A isotherms are qualitatively consistent with the published results[1,3,8]. The π-A isotherms of the *a*- and *s*-PMMAs show similar tendencies and an inflection point at about 17.5 mNm^{-1}. However, that of the *i*-PMMA shows two inflection points at about 8 and 17.5 mNm^{-1} and long tail at the surface pressure lower than the first inflection point. Hysteresis was found for all the monolayers of stereoregular PMMAs if they were compressed above the inflection points and then released. However, if compressed below the inflection points and then released, no hysteresis was observed.

The surface potentials of the *a*- (Fig. 1(a)) and *s*-PMMAs (Fig. 1(b)) increase rapidly from zero even in the region where $\pi = 0$. In the region where π increases from 0, the surface potentials increase but with slower rate. The apparent dipole moments increase rapidly in the region where $\pi = 0$ and reach the maximum values of 0.24 and 0.19 Debye (D) for *a*- and *s*-PMMAs, respectively, at the region where the surface pressure begins to rise, and then decrease upon further compression. On the contrary, the surface potential of the *i*-PMMA (Fig. 1(c)) increases linearly in the region where the surface pressure is lower than the first inflection point. In this



(a)

(b)

(c)

FIGURE 1 Surface pressure, surface potential and apparent dipole moment of monolayers of (a) *a*-PMMA, (b) *s*-PMMA and (c) *i*-PMMAs.

region, the apparent dipole moment is nearly constant with 0.23 D. The surface potential and apparent dipole moment above the first inflection point show the similar trends as *a*- and *s*-PMMAs in the region where $\pi > 0$.

Figure 2(a), (b) and (c) show plots of average transfer ratio *versus* transfer pressure for the *a*-, *s*- and *i*-PMMAs, respectively, transferred onto all the substrates except the glass substrate. The average was taken for 12 - 24 layers, where transfer ratio is defined as the ratio of monolayer area lost to the area swept by the substrate as usual. Films transferred onto the Al and Cr substrates during the first upward stroke were baked as described in the experimental section. If not baked, the films were peeled off during the next downward stroke. However, the baking was not required for Au and Si substrates.

All of the stereoregular PMMA LB films show similar trend in transfer characteristics with respect to the transfer pressure. Z-type multilayers were formed at a transfer pressure below 1 mNm^{-1} for *a*- and *s*-PMMAs and 5 mNm^{-1} for *i*-PMMA. Z-type transfer at these low pressures was maintained even after more than 20 strokes as shown in Fig. 3. The average transfer ratio of the downward stroke increases as the transfer pressure increases from those values, reaching a maximum at the transfer pressure of 10 mNm^{-1} for the *a*-PMMA and *s*-PMMAs and at 15 mNm^{-1} for the *i*-PMMA. The average transfer ratios of both the downward and upward stroke decrease as the transfer pressure increases above the transfer pressures corresponding to the maximum of downward stroke.

The thickness of the PMMA LB films was measured with an ellipsometry (Auto EL, Rudolph Reseach) for various number of layers and the monolayer thickness was calculated from the slope of the thickness *versus* number of layers. The measured monolayer thickness of the Y-type LB films of the *a*-, *s*- and *i*-PMMAs were 9.6, 9.4 and 9.9 Å, respectively, which are a little different from the reported values of 8.5 Å (15 mNm^{-1}) for *a*-PMMA[1] and 9.1 Å (10 mNm^{-1}) for *s*-PMMA[15]. Interestingly enough, when the monolayers were transferred at 15 mNm^{-1} for *a*- and *s*-PMMAs and 20 mNm^{-1} for *i*-PMMA where the transfer ratios are much lower than 1, the monolayer thicknesses were almost the same or larger than the Y-type films with the values of 9.4 Å for *a*- and *s*-PMMAs and 11.4 Å for *i*-PMMA. Especially the increase was higher in the *i*-PMMA LB films.

The effect of substrates on the transfer characteristics is not significant, as

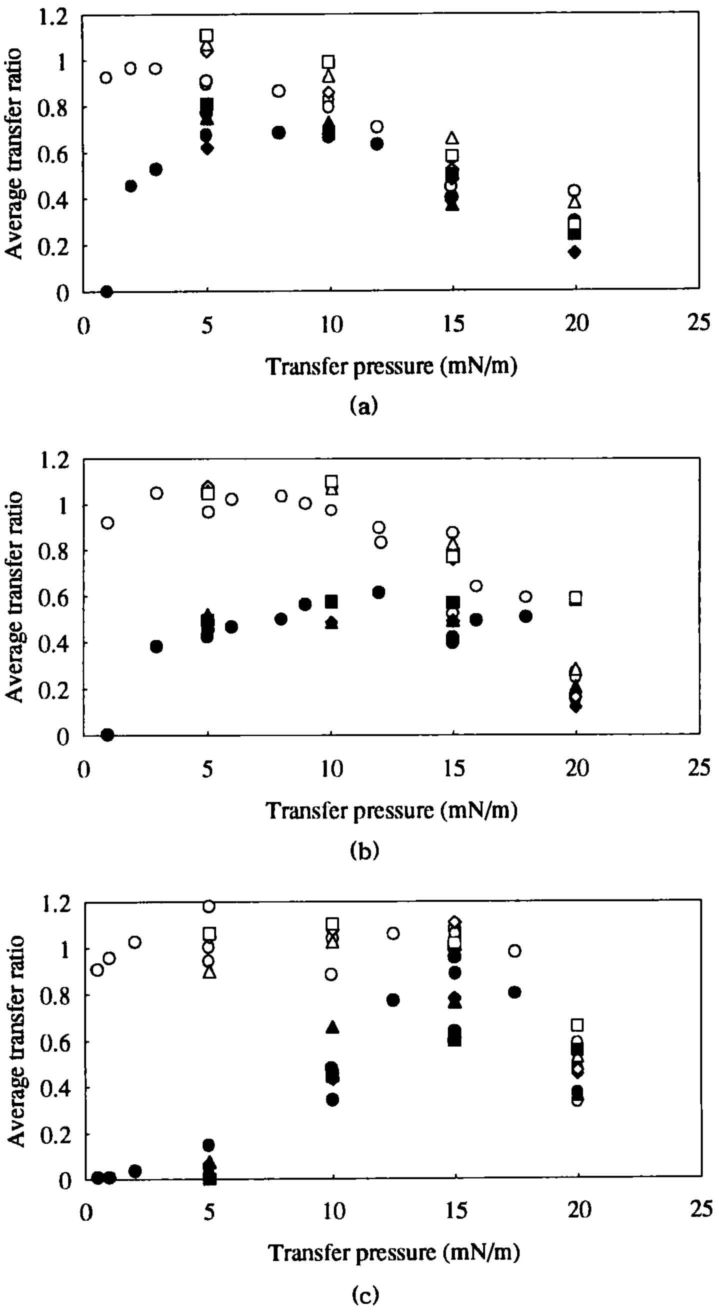


FIGURE 2 Average transfer ratio of (a) *a*-PMMA, (b) *s*-PMMA and (c) *i*-PMMA transferred onto the Al(□,■), Cr(◇,◆), Au(△,▲) and Si(○,●), where the open and closed symbols represent the upward and downward strokes, respectively.

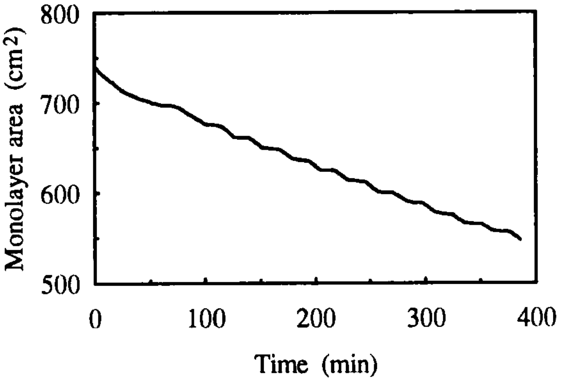


FIGURE 3 A stepwise decrease of monolayer area representing the formation of Z-type LB film; *i*-PMMA transferred onto Au substrate at 5 mNm^{-1}.

shown in the Fig. 2, except for the glass substrate. The glass substrate shows quite a different transfer characteristics from the other substrates. The layers transferred during the first upward stroke were peeled off during the next downward stroke even though they were baked up to 150 ℃. This result is also quite different from that obtained by Stroeve *et al.*[3] They obtained Z-type multilayers of s-PMMA on the glass substrate at the transfer pressure of 12 mNm^{-1}. However, we can hardly explain the difference just by comparing the published experimental details[3] to ours. From these results, the presence of critical hydrophilicity or contact angle of the substrate above which mulilayers are obtainable could be anticipated.

DISCUSSION

The gradual change of the transfer characteristics from the Z-type to the Y-type with increasing transfer pressure may be explained in terms of packing density as Clint and Walker[16] described. As the packing density increases, the hydrophobicity of the surface of the substrate formed after upward stroke is expected to increase. As a result, the hydrophobic interaction between the substrate and monolayer during the following downward stroke increases, and thus the transfer ratio increases. The rather gradual increase in the transfer ratio during the downward stroke of the *i*-PMMA may be due to the expanded nature of the material.

Along with the packing density, it may be informative to consider molecular arrangement in the floating monolayers. Comparison of results of apparent dipole moments (Fig. 1(a) and (b)) and transfers (Fig. 2(a) and (b)) for *a*- and *s*-PMMAs indicates that Z-type structure is formed around the surface pressure corresponding to the maximum apparent dipole moment. As the surface pressure increases, the apparent dipole moment decreases and the downward transfer ratio increases.

For the transfer of monolayers during the downward stroke, not only the packing density but also the interactions between hydrophilic groups of the chains and water molecules and lateral interactions between the chains may play an important role. Considering the largest contribution of bond dipole moment of C=O (2.04 D[17]) bond to the molecular dipole moment and the little differences in the maximum values of the apparent dipole moments for all the stereoregular PMMAs, it is judged that in the region of maximum apparent dipole moment the C=O bond may be aligned in the direction normal to the air/water interface. Because of the strong hydrogen bonding between the oxygen atom in the C=O bond and water molecules, chains may keep in contact with the water surface. In this region, interactions between the hydrophobic surfaces of transferred layer and the floating monolayer can be weaker than that between the hydrophilic parts of floating monolayer and water molecules during the downward stroke. Consequently, no transfer can take place during the downstroke and hence the formation of Z-type stucture is possible.

In the region where the apparent dipole moment decreases with increasing surface pressure, the chains can laterally interact with each other and rearrange themselves resulting for the C=O bond to be aligned less normal to the water surface. The lateral interactions and the less normal direction of the C=O bond may result in the reduction of the interactions between the hyrdophilic groups and the water molecules. The more the chains are interacting, the weaker the interactions between the hydrophilic groups and the water molecules, hence the transfer of monolayers during the downward stroke seems to be possible.

The apparent dipole moment of *i*-PMMA maintains higher values in the region of surface pressure below 5 $\mathrm{mNm^{-1}}$ where Z-type structure is formed as shown in the Fig. 1(c) and Fig. 2(c). The expanded monolayer characteristics, the high value of the apparent dipole moment and the same position of the pendant groups in the backbone suggest that the chains lie in the form of horizontal disposition with the hydrophilic ester groups touching the water surface[12]. As for the *a*- and *s*-PMMAs, Z-type structure can be formed in the region of higher apparent dipole moment, and the increase in the upward transfer ratio with increasing transfer pressure can also be explicable with the same reasons. The formation of Z-type multilayers of *i*-PMMA maintained at the higher transfer pressure (5 $\mathrm{mNm^{-1}}$) compared to the other PMMAs (1 $\mathrm{mNm^{-1}}$) and the gradual increase in the downward transfer ratio seem to be due to the higher concentration of hydrophilic groups touching the water surface resulting from the high flexibility of chains of the *i*-PMMA[18].

The downward and upward transfer ratios decreased as the transfer pressure increased above 10 $\mathrm{mNm^{-1}}$ for the *a*- and *s*-PMMAs and 15 $\mathrm{mNm^{-1}}$ for the *i*-PMMA. Packing density alone is not enough to explain this result. The monolayer thicknesses of LB films of *a*- and *s*-PMMAs transferred at the transfer pressure of 15 $\mathrm{mNm^{-1}}$ and *i*-PMMA at 20 $\mathrm{mNm^{-1}}$ were almost the same or larger than those transferred at 10, 12 and 15 $\mathrm{mNm^{-1}}$, respectively. From the results of monolayer thickness, it seems that formation of loops or crossing of the chains is attributable to the decrease in the transfer ratio with increasing transfer pressure. However, more detailed informations on the monolayer configurations are required to explain these results.

CONCLUSION

Systematic investigations of the effects of the transfer pressure, types of the substrates and stereoregularity on the transfer characteristics of the stereoregular PMMAs were performed in terms of the average transfer ratio. All of the stereoregular PMMA monolayers showed similar trend in transfer characteristics with respect to the transfer pressure. Z-type multilayers were formed at the transfer pressure below 1 $\mathrm{mNm^{-1}}$ for the *a*- and *s*-PMMAs and 5 $\mathrm{mNm^{-1}}$ for the *i*-PMMA, respectively. The average transfer ratio of the downward stroke increased as the transfer pressure increased from those values, forming Y-type multilayers at the transfer pressure of 10 $\mathrm{mNm^{-1}}$ for the *a*- and *s*-PMMAs and at 15 $\mathrm{mNm^{-1}}$ for the *i*-PMMA. The effect of the types of the substrate on the transfer characteristics was not significant except for the glass substrate when the first layers were baked. The molecular arrangement of the floating monolayers deduced from the apparent dipole moment was found to be informative in interpreting the transfer characteristics of LB films of stereoregular PMMAs.

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