Poly(*N*-alkylmethacrylamide) LB Films with Short-Branched Alkyl Side Chains for a Self-Developed Positive Photoresist

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ABSTRACT: An ultrathin film of poly(*N*-neopentylmethacrylamide) (PnPMA) prepared by the Langmuir−Blodgett technique was examined as a high-resolution self-developed photoresist. The properties of the LB films were investigated using UV absorption spectra and X-ray diffraction. Fine lines and spaces with positive-tone patterns on the LB film were achieved solely by deep UV irradiation (self-development). A fine gold pattern with a resolution of 1.5 μm was obtained by etching patterned LB film on gold film deposited on a glass substrate, indicating that 20 layers of LB film (about 20 nm) is stable against wet etching.

Introduction

To meet increasing demands for photolithography to show smaller features, the tools used for exposure are progressing from the g line (436 nm) to the I line (365 nm) and are moving to deep UV (248−193 nm) sources.[1] However, appropriate resist materials must be developed so that the high performance of these tools can be realized.

Thin, high-quality resist films with no defect and a smooth surface may yield high resolution in lithography. However, various efforts to realize the high resolution are becoming limited by the resolution of current imaging technology based on spin-coat films. Features with dimensions below 100 nm are difficult to resolve. We have continued to investigate the application of Langmuir−Blodgett (LB) films to a new resist film instead of using conventional spin-coat films.[2−8] Since the LB technique is one of the most effective ways of forming a molecularly ordered ultrathin film of controlled thickness and orientation, LB films should realize ultrahigh-resolution photolithography.[9−12] Barraud et al. obtained fine negative patterns on LB film by electron beam polymerization using ω-tricosenoic acid.[13] Ringsdorf et al. studied the photopolymerization of octadiene and docosadiene derivatives.[14] Furthermore, Fu et al. investigated fine negative patterns of PMMA LB films using electron beam irradiation.[15]

In the previous work,[8] we found that poly(*N*-tetradecylmethacrylamide) (PTDMA) forms a stable monolayer and LB film, and furthermore this LB film decomposes upon exposure to UV irradiation. Thus, the LB film could function as a novel self-developable positive photoresist. The sensitivity of PTDMA LB film to UV irradiation increases with decreasing number of layers in the film. We also found that poly(*N*-*tert*-pentylacrylamide), which has a short-branched pendant side chain instead of a long alkyl (dodecyl chain), gives polymer LB film with a thickness of ca. 1.0 nm.[16]

The present study investigates the monolayer behaviors and LB film formation of several poly(*N*-alkylmethacrylamide)s with short-branched alkyl side chains to obtain thinner polymer LB films that self-decompose. The photolithography property of the polymer LB films is evaluated. A fine pattern on gold film with a resolution of 1.5 μm was obtained by etching a gold film using the patterned PnPMA LB film as the resist.

Experimental Section

Materials. All of *N*-alkylmethacrylamide monomers (alkyl substituent: *tert*-butyl (tBMA), *tert*-pentyl (tPMA), neopentyl (nPMA), isopentyl (iPMA)) were synthesized by the reaction of methylacryloyl chloride and the corresponding alkylamine in the presence of triethylamine in dried chloroform. A mixture of alkylamine, triethylamine, and dried chloroform was cooled to 0 °C in a water bath containing ice. Methylacryloyl chloride was then added dropwise to the mixture while stirring, and then the mixture was allowed to stand at room temperature for 48 h. Thereafter, the mixture was washed with dilute hydrochloric acid, followed by $NaHCO_3$ aqueous solution (10% w/v), and finally with water. The chloroform layer was dried over anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by column chromatography.

Poly(*N*-alkylmethacrylamide)s with various short-branched alkyl substituents (Figure 1) were prepared in dried benzene at 60 °C by free-radical polymerization using AIBN as a thermal initiator. The polymers were purified by dissolution in chloroform, filtration, and precipitation into a large excess of hexane three times and then dried under vacuum at room temperature. Their molecular weights and polydispersity values for poly(*N*-*tert*-butylmethacrylamide) (PtBMA), poly(*N*-*tert*-pentylmethacrylamide) (PtPMA), poly(*N*-neopentylmethacrylamide) (PnPMA), and poly(*N*-isopentylmethacrylamide) (PiPMA) were 1.62×10^4 ($M_w/M_n = 1.63$), 8.07×10^4 (1.94), 1.93×10^4 (1.66), and 3.62×10^4 (1.85), respectively.

Monolayer and Multilayer Formation. Measurement of surface pressure (π)−surface area (A) isotherms and the deposition of monolayer were carried out with a computer-controlled Langmuir trough (FSD-110, USI) at a compression speed of 14 cm^2/min. Distilled, deionized water with a resistivity above 17 MΩ·cm was used as the subphase. Spectroscopic grade chloroform was used to spread monolayers on the water surface. Quartz, glass, and silicon substrates for the deposition of monolayers were cleaned in a boiling concentrated HNO_3 and rendered hydrophobic with *n*-octyltrichlorosilane. The gold film on a glass substrate was evaporated using a Hitachi E101 ion sputter in high vacuum. Before the gold film deposition, the glass substrate was rendered hydrophobic with *n*-octadecyltrichlorosilane. A mixture of I_2 (0.6 g), NH_4I (1.5 g), ethanol (20 mL), and pure water (30 mL) was used as the etchant, and the etching time was 20 s.

Measurement. The molecular weights of the polymers were determined by a Toyo Soda HLC-802A gel permeation chromatography (GPC) using a polystyrene standard. The UV

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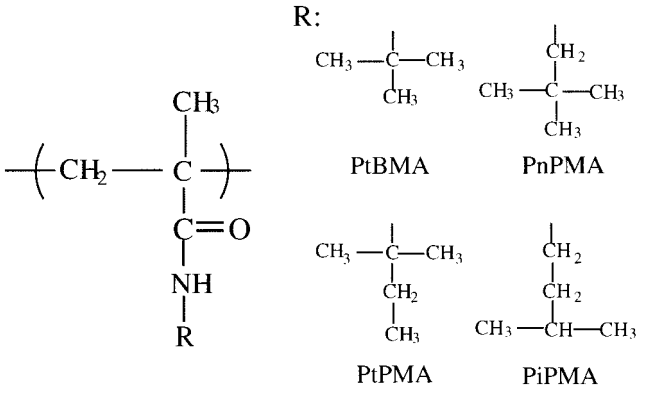

Figure 1. Chemical structure of poly(*N*-alkylmethacrylamide)s with short-branched side chains.

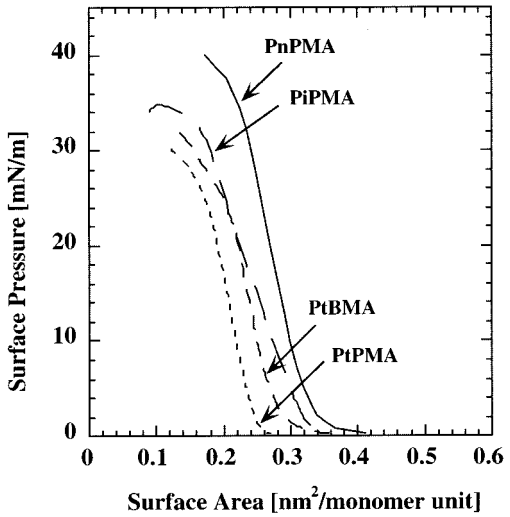

Figure 2. Surface pressure−area isotherms of poly(*N*-alkylmethacrylamide)s with short-branched side chains (the reproducible isotherm curves were obtained in repeat measurements).

absorption spectra were measured using a Hitachi U-3000 UV−vis spectrophotometer. The thickness of the LB films was determined by a Sloan Dektak 3ST surface profile. Resist patterns and gold film patterns were observed by an Olympus VANOX-T microscope. The XRD was carried out by M18XHF[22]-SRA, and the wavelength $\lambda = 0.1541$ nm (Cu Kα) was used. Deep UV irradiation was carried out with a high-pressure Hg lamp (UXM-501MD) using a water filter.

Results and Discussion

Monolayer Behavior on the Water Surface. Poly(*N*-alkylmethacrylamide)s with various short-branched alkyl chains were spread from a chloroform solution onto the water surface to measure $\pi-A$ isotherms at 15 °C (Figure 2). Obviously, all the $\pi-A$ isotherms show a steep rise in surface pressure and have a high collapse pressure, suggesting that these polymers formed stable monolayers on the water surface in the same manner as poly(*N*-tetradecylmethacrylamide).[8] The isotherms apparently vary with alkyl side chains, and the most stable monolayer is obtained with PnPMA. Polymer monolayers with short straight alkyl chains form an expanded form owing to insufficient cohesive force between alkyl substituents.[17] Apparently, the branched alkyl chain is more useful for monolayer formation than long alkyl substituents of the same chain length. A PnPMA monolayer results in a higher collapse pressure than a PTDMA monolayer.

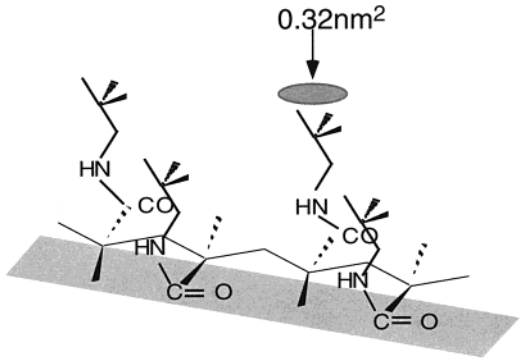

Figure 3. Schematic illustration of orientation of alkyl side chains in condensed monolayer.

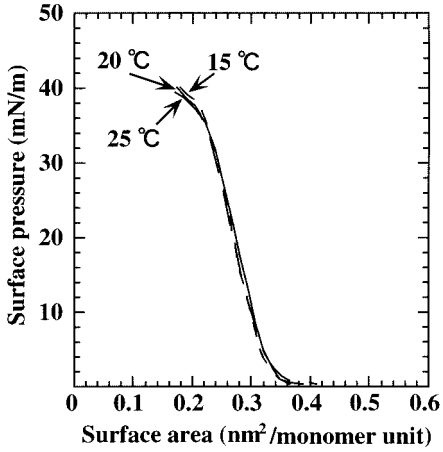

Figure 4. Surface pressure−area isotherms of PnPMA at varioust subphase temperatures.

The limiting surface area per monomer unit was determined by extrapolating the linear portion of steep rise in the $\pi-A$ isotherms to zero surface pressure. The estimated surface area of PnPMA is 0.32 nm^2, which is consistent with the cross section calculated from the CPK model based on the condensed packing (Figure 3). This is similar to the reported value of poly(*N*-neopentylacrylamide).[16]

Figure 4 shows $\pi-A$ isotherms of the PnPMA monolayer at various subphase temperatures. The $\pi-A$ isotherms did not significantly depend on temperature. This indicates that the packing of the short-branched alkyl chains is not such an important factor for stable monolayer formation, which is different from the monolayer composed of long alkyl chain derivatives. Since PnPMA formed the most stable monolayer among the investigated polymers, subsequent experiments mainly used PnPMA.

LB Film Formation. The condensed monolayer of these polymers on the water surface can be transferred onto hydrophobic substrates, such as quartz, glass, and silicon wafer as a Y-type LB film under a given surface pressure. The transfer ratios in both downward and upward strokes are summarized in Table 1. Apparently, both transfer ratios are almost unity except for PtBMA. Moreover, the transfer ratio of the downward stroke was slightly smaller than that of upward stroke. This was caused by the weak cooperative hydrophobic interaction between short-branched alkyl substituents relative to the cooperative hydrophilic interaction of the amide groups. Thus, the deposition of the polymer monolayers on a hydrophobic surface should become less efficient.

Table 1. Transfer Condition and Transfer Ratio of Poly(*N*-alkylmethacrylamide)s

polymer	transfer ratio		pressure for deposition (mN/m)
	downward	upward	
PtBMA	0.65 ± 0.05	0.75 ± 0.05	18
PtPMA	0.85 ± 0.05	0.94 ± 0.05	18
PnPMA	0.94 ± 0.05	0.98 ± 0.05	22
PiPMA	0.83 ± 0.05	0.91 ± 0.05	20

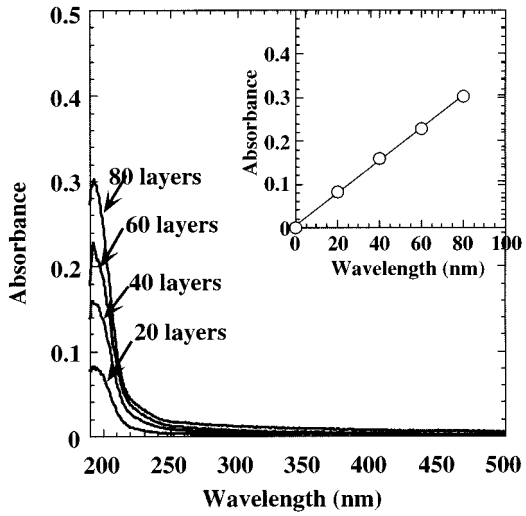

Figure 5. Absorption spectra of PnPMA LB film with several deposited layers. Inset: linear relationship between absorbance and number of layers.

The transfer ratios for a PnPMA monolayer measured at various surface pressures of 15, 18, and 22 mN/m were 0.70, 0.91, and 0.96, respectively. Monolayer deposition at higher surface pressure improves the transfer ratio.

The UV absorption spectra of the PnPMA LB film were measured as a function of the number of deposited layers (Figure 5). The maximal absorbance at 193 nm was proportional to the number of layers at least up to 80 layers. The linear relationship between the absorbance and the number of layers suggests regular homogeneous deposition of the PnPMA monolayer. The absorbance per one layer (D) calculated from the slope of the straight line in Figure 5 (the inserted) was 3.82×10^{-3}. Moreover, the molar extinction coefficient (ϵ) of PnPMA was 7.36×10^3 (mol/L)$^{-1}$ cm^{-1} determined from the Lambert−Beer equation: $D = 1.66 \times 10^{-7} \epsilon S$, where S is the molecular density (molecules/cm^2).

The layer structure and the LB film thickness of PnPMA LB film were investigated by X-ray diffraction measurement. The XRD pattern of a 40-layer PnPMA LB film has Kiessig fringes caused by interface reflection and one Bragg peak caused by periodic bilayers as shown in Figure 6. The thickness of the monolayer determined from the Bragg peaks was 0.94 nm. The overall film thickness determined from the constant spacing of the Kiessig fringes[16] was 38.6 nm, which agrees quite well with the thickness obtained from multiplying the number of transferred layers (40) by the layer periodicity (0.94 nm). These results also precisely agree with the film thickness estimated from the CPK model, where the short-branched alkyl substituents are oriented perpendicular to the LB film surface. Furthermore, the appearance of defined Kiessig fringes indicates that the LB film has a highly ordered layer structure with constant periodicity. This result suggests the formation of regular homogeneous LB film.

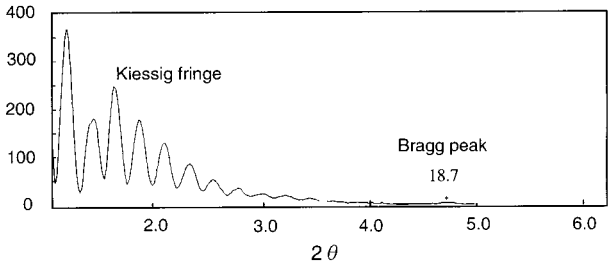

Figure 6. X-ray diffraction patterns of PnPMA LB film with 40 deposited layers.

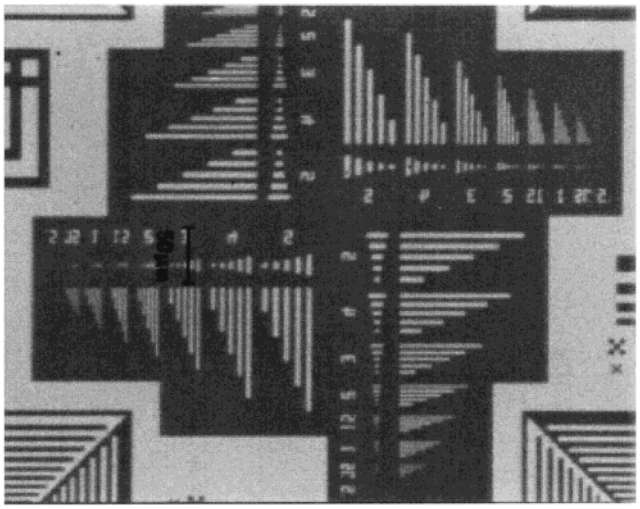

Figure 7. Optical micrograph of positive fine patterns using PnPMA LB film (20 layers) deposited on a gold film evaporated on a glass substrate after deep UV irradiation without development.

Drawing Fine Patterns on the PnPMA LB Film. Twenty layers of PnPMA LB film deposited on a gold film were irradiated with deep UV light from a high-pressure Hg lamp in air through a photomask figured with a test pattern. The result is shown in Figure 7. Fine patterns with a resolution of 0.75 μm, which is the highest resolution in the mask employed in the present study, were produced on the PnPMA LB films without any development (self-development). This finding showed that PnPMA LB film can be as effectively decomposed by deep UV irradiation as PTDMA LB film.[8]

Figure 8 shows the sensitivity curves of PnPMA LB films with various numbers of layers. The normalized film thickness decreased with increasing exposure time. Moreover, the sensitivity was remarkably enhanced by decreasing number of layers. The shape of plots in Figure 8 indicates that the contrast values of PnPMA LB films with 80, 100, and 120 layers were 3.7, 2.8, and 1.5, respectively. The PnPMA LB film was more sensitive than PTDMA LB film with the same number of deposited layers. This is because the thickness of PnPMA LB film is thinner than that of PTDMA LB film with the same number of deposited layers.

Pattern Fabrication on Gold Film. Patterns on a gold film were resolved by an etching process using the patterned PnPMA LB film as the resist. First, fine photopatterns were drawn on a PnPMA LB film with 20 layers deposited on a gold film by direct deep UV irradiation, and then the substrate was etched for 20 s in a mixture of 1.5 g of NH_4I, 0.6 g of I_2, 20 mL of ethanol, and 30 mL of H_2O. Finally, the resist film was removed from the substrate using chloroform. The

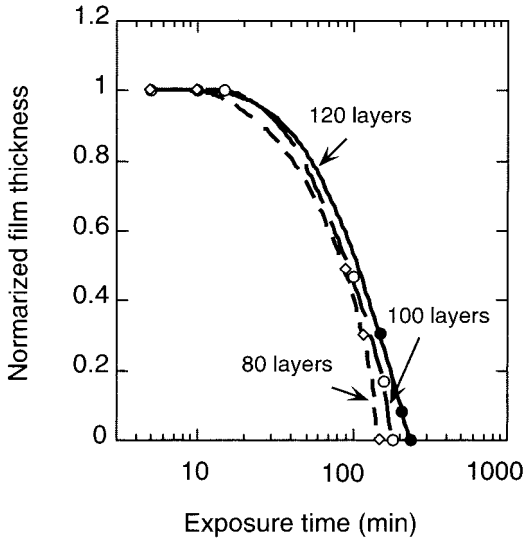

Figure 8. Sensitivity curves of PnPMA LB films with various numbers of deposited layers for deep UV irradiation.

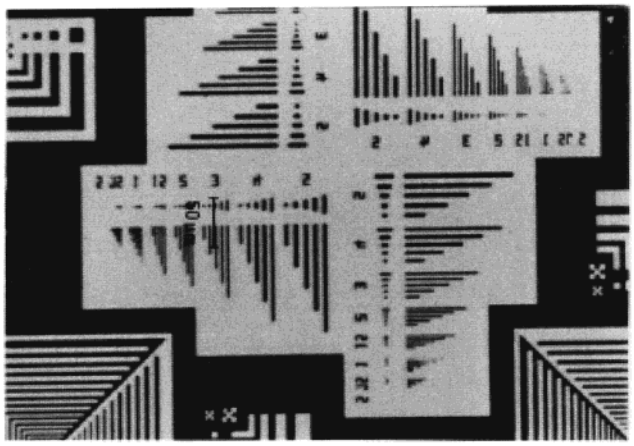

Figure 9. Patterns on gold film fabricated by etching.

remaining patterns of gold film were observed with an optical microscope (Figure 9), which can transfer an image with a resolution of 1.5 μm. These results indicate that a 20-layer PnPMA LB film (about 20 nm thick) provides good resistance to the etchant. Therefore, LB film has a potential application to microfabrication. When less than six layers of LB film are deposited, etching resistance was poor and fine patterns could not be transferred. This lithographic property suggests that PnPMA LB film should be applicable to new self-developable positive photoresist.

Conclusion

Several amphiphilic poly(alkylmethacrylamide)s with different short-branched alkyl chains were prepared. Of these, PnPMA formed the most stable monolayer on the water surface. Condensed monolayers of PnPMA were transferred onto solid substrates at a given surface pressure, forming regular homogeneous Y-type LB films.

Fine positive patterns on PnPMA LB film with a resolution of 0.75 μm were self-developed by deep UV irradiation from a high-pressure Hg lamp. The sensitivity of PnPMA LB film was enhanced by decreasing the thickness of the PnPMA LB film. The sensitivity of PnPMA LB film was higher than that of the PTDMA LB film with the same number of deposited layers. PnPMA LB film with only 20 deposited layers provided a good etching resistance, and a fine pattern with a resolution of 1.5 μm was transferred to a gold film from the patterned LB film.

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