# Headline Articles

## An Environmentally Friendly Water-Developable Positive Photoresist Using LB Films Fabricated from Methacrylamide Copolymers

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A water-developable photoresist system based on deep UV irradiation was prepared from the copolymer LB films of *N*-(2,2-dimethylpropyl)methacrylamide (DMA) and *N*-phenylmethacrylamide (PhMA). The copolymers with different compositions form stable monolayers on the water surface. These monolayers can be transferred successively onto solid supports by both downward and upward strokes, yielding Y-type uniform polymer LB films. On deep UV irradiation, the LB films decompose effectively and become water-soluble. After development with pure water, the fine positive resist patterns based on the unexposed parts can be drawn. A water-developable positive resist with polymer LB film was prepared for the first time.

In lithographic processes, resist materials have been deemed as one of the key materials to obtain high-resolution lithography. Thus, there has been an increasing interest in designing and developing a new type of resist materials. A number of new resist or imaging materials exhibiting high sensitivity and high resolution have been developed in recent years.[1—3]

Various lithographic techniques such as deep UV light,[4] electron beams,[5] and X-rays,[6] have been investigated to realize a high resist resolution. The application of scanning tunneling microscope (STM) is a new technique for ultrafine patterning drawing.[7,8] These techniques have been proposed as possible exposure systems for the next generation of high-resolution lithography. Instead of conventional spin-coated polymer films, more elaborate films such as self-assembled monolayers (SAMs) and LB films have been employed for realizing high-resolution lithography. SAMs have often been used to draw ultra-fine pattern because a well-defined monolayer on substrates with self-organization properties can be easily fabricated. Whitesides and co-workers presented a molecular stamping method using alkanethiol to a gold substrate.[9] Crooks and co-workers also investigated the polymeric self-assembling monolayers of diacetylenic alkanethiol using UV irradiation.[10]

The Langmuir–Blodgett (LB) technique has been approved as an effective way to form a defect-free and molecularly ordered ultrathin film with controlled thickness and orientation.[11,12] Because the LB technique can overcome the weakness of spin-coat films in which molecules are distributed randomly, the polymer LB films have recently been investigated. Researchers want high resolution lithographic resists with electron beams or X-ray beams to expose the resist layers deposited on substrates and then a development process to remove the exposed portions (positive type) or the unexposed portions (negative type) selectively.[13—16]

Previously, we have succeeded in the preparation of fairly uniform polymer LB films using acrylamide polymers having long alkyl chains.[17] Furthermore, we also succeeded in producing the fine patterns by the polymerization of *N*-alkylacrylamide monomer LB films[18,19] and the cross-linking reaction in polymer LB films[20] with UV irradiation and electron beam.[21] All of these LB films resulted in negative photoresists. Recently, we have reported a new type of positive photoresist using poly(*N*-tetradecylmethacrylamide) LB film without any development process (we also call it dry-development).[22,23]

In the process of conventional lithography, various organic solvents were used as developers in the development step. The use of organic developers not only causes a resist pattern swelling and collapse but also represents a serious environmental health and safety concern. Recently, a few investigations about water-developable resists have been carried out.[24—26] Ichimura reported that substitution of a very small fraction (<3 mol%) of styrylpyridinium or quinolinium groups on poly(vinyl alcohol) resulted in water-soluble negative resists.[24] Willson and co-workers proposed a water-developable negative photoresist system with three water-soluble components, which gave a resolution of 1 μm.[25] There is no water developable resist using Langmuir–Blodgett film so far.

In the present paper, we describe a new type of water-developable positive photoresist system with the copolymer LB films of *N*-(2,2-dimethylpropyl)methacrylamide, which is found to have an ability of stable monolayer formation, and *N*-phenylmethacrylamide, which has an absorption maximum at 245 nm. With deep UV irradiation, the LB films could decompose effectively and become water-soluble. After the resists were developed in water, a fine pattern with a resolution of 0.75 μm, which is the highest resolution of the photomask employed in this study, was clearly drawn. A water-developable positive resist with polymer LB film was prepared for the first time.

## Experimental

**Materials.** *N*-(2,2-Dimethylpropyl)methacrylamide (DMA) monomer was synthesized by reaction of methacryloyl chloride and 2,2-dimethylpropylamine in the presence of triethylamine in chloroform and purified by column chromatography. *N*-Phenylmethacrylamide (PhMA) monomer was synthesized by reaction of methacryloyl chloride and aniline in the presence of triethylamine and 4-dimethylaminopyridine (as the catalyst) in chloroform and purified by column chromatography.

Copolymers with various compositions of DMA and PhMA monomer units (Fig. 1) were prepared by free-radical polymerization at 60 °C in dried toluene using AIBN as a thermal initiator. The copolymers were purified by dissolution in toluene, filtering, and precipitation into a large excess of hexane with two times, and subsequently dried under vacuum at room temperature. The molecular weights and polydispersities for COP11, COP24, COP30, and COP45 are $2.23\times10^4$ ($M_w/M_n$ = 1.88), $2.24\times10^4$ (1.87), $1.80\times10^4$ (2.12), and $3.14\times10^4$ (2.34), respectively. In the same way, poly[*N*-(2,2-dimethylpropyl)methacrylamide] (HOMP) was also obtained, with a molecular weight of $1.93\times10^4$ (1.66).

**Monolayer and Multilayer Formation.** Measurement of surface pressure ($\pi$)-surface area ($A$) isotherms and deposition of monolayers were carried out with a computer-controlled Langmuir trough (FSD-110, USI). Distilled and deionized water with resistivity values higher than 17 MΩ cm$^{-1}$ was used as the subphase. Chloroform used for spreading monolayers on the water surface was of spectroscopic grade. Quartz and silicon substrates for deposition of monolayers were cleaned in boiling concentrated $HNO_3$ and made hydrophobic with trichloro(octadecyl)silane.

**Measurement.** The molecular weights were determined by a Toyo Soda gel permeation chromatography (GPC) using a polystyrene standard. The copolymer compositions were determined by $^1$H NMR spectroscopy. UV absorption spectra were recorded with a Hitachi U-3000 UV-visible spectrophotometer. The thickness of each LB film was determined by the surface profilometry using a Sloan Dektak 3ST. Deep UV irradiation was carried out with a high-pressure Hg lamp (Ushio UXM-501MD) using a water filter.

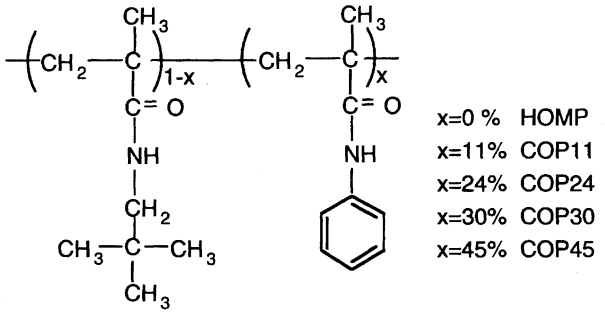


Fig. 1. Chemical structure of the copolymers.

## Results and Discussion

**Monolayer Behavior on the Water Surface and LB Film Formation.** The copolymers with various compositions of the monomer units were spread on a water surface from a chloroform solution to measure the pressure ($\pi$)-area ($A$) isotherms 15 °C. The isotherms indicate that all of the copolymers form stable monolayers with a steep rise in surface pressure and a relatively high collapse pressure (Fig. 2). The isotherms are shifted toward a region of smaller surface area with increasing mole fraction of PhMA units. The average molecular occupied surface area per repeat unit is estimated by extrapolating the steep rising part of the $\pi$–$A$ curves to zero pressure. The surface areas for the copolymers were obtained to be 0.31, 0.29, 0.28, and 0.25 nm$^2$/repeat unit for COP11, COP24, COP30, and COP45, respectively. The plots of the surface area against the mole fraction of PhMA give a good linearity (Fig. 3), which indicates that the average surface area of the monolayers is determined by an additional rule in the surface area of PhMA and DMA monomer, that is, the monomer units behave as an ideal mixing of the copolymer monolayers. The collapse pressures for the copolymer monolayers also decrease with the mole fraction of PhMA, which is consistent with an ideal mixing behavior. From the linear relationship in Fig. 3, the surface area of PhMA homopolymer monolayer, which cannot actually exist as a stable form on the water surface, can be estimated to be approximately 0.16 nm$^2$/monomer unit. This value is consistent with the area calculated from the CPK model of a phenyl ring (Fig. 4) and also with the value reported in the previous study on the monolayer of poly(*N*-dodecylacrylamide-*co*-styrene).[27] On the basis of the results, we propose the orientation of the copolymer monolayers on

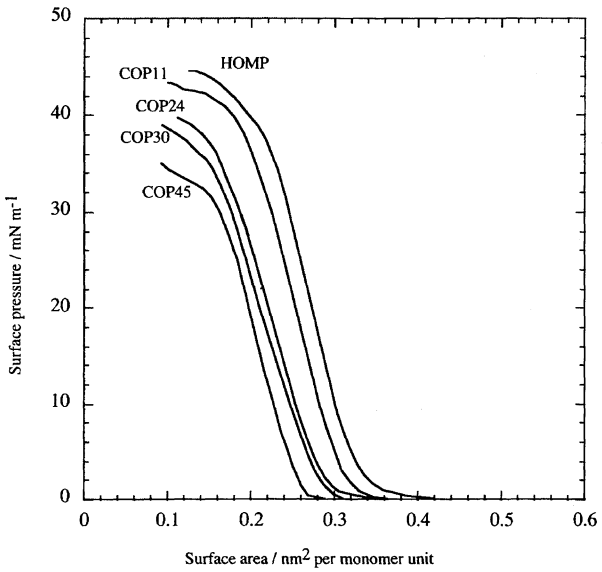


Fig. 2. Surface pressure-area isotherms of the copolymers on the water surface at 20 °C with a compression rate of 14 nm$^2$ min$^{-1}$.

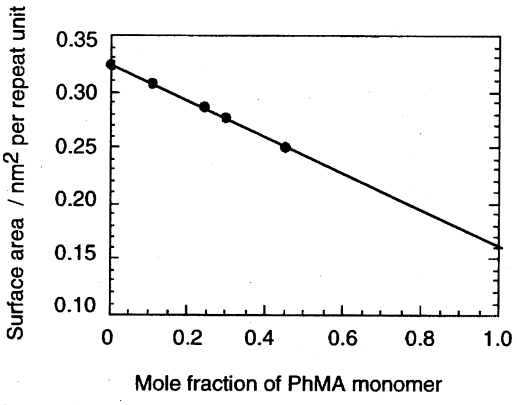


Fig. 3. Molecular occupied surface area as a function of mole fraction of PhMA.

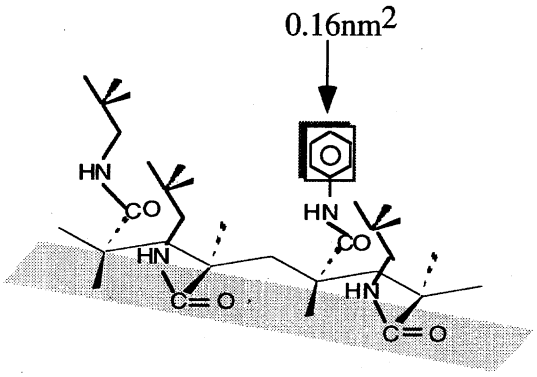


Fig. 4. Probable orientation of the copolymer monolayer on the water surface.

the water surface as shown in Fig. 4, where the polymer main chain is laid horizontally on the water surface and the phenyl rings are oriented perpendicular to the chain.

The condensed copolymer nomolayers on the water surface can be transferred onto solid supports such as glass, quartz, and silicon wafer under a certain surface pressure, yielding Y-type LB films. The transfer behavior of the copolymer monolayers were examined with UV-visible spectra. Figure 5 shows the UV absorption spectra of the COP30 LB films deposited at 20 mN $m^{-1}$ as a function of the number of deposited layers. The absorbances at 201 and 245 nm are proportional to the number of layers at least up to 80 layers (inserted in Fig. 5). The linear relationship between the absorbance and the number of layers suggests that a regular deposition of the COP30 monolayer takes place, resulting in a fairly uniform LB film. The total average transfer ratios of the upward stroke and downward stroke up to 80 layers were maintained at 1.0±0.1 and 0.9±0.1, respectively. Although the UV-visible spectra of the COP45 LB film as a function of the deposited number also show a linear relationship for the LB films with less than 40 layers, the absorbance gradually deviated from the line when the number of layers exceeds 40 layers. This is due to a gradual decrease in the transfer ratio for the downward stroke, which indicates that the transferability of the copolymer monolayers decreases with increasing mole fraction of PhMA units. Thus, we can prepare fairly uniform polymer LB films from the copolymers of

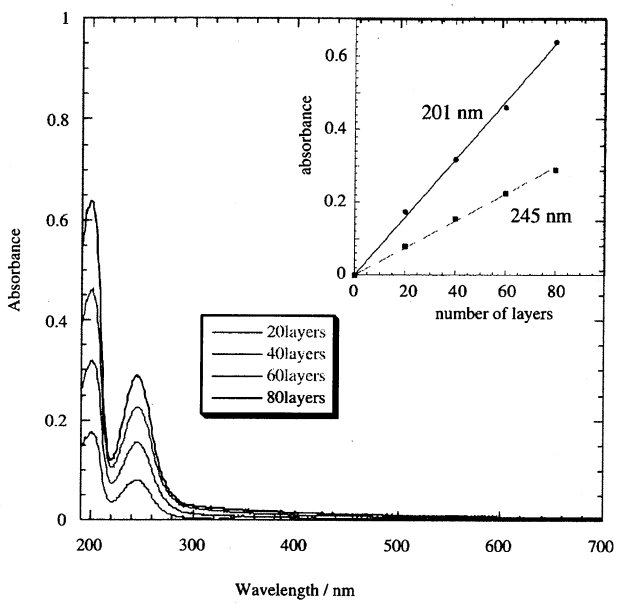


Fig. 5. Absorption spectra of the COP30 LB film with the number of layers deposited; Inserted: A linear relationship between absorbance and number of layers.

DMA and PhMA, depending on the mole fraction of PhMA and the number of layers.

**Drawing Fine Patterns on the Copolymer LB film.** The monolayer of COP30 was transferred onto a silicon wafer with 70 layers, on which deep UV light from a high-pressure Hg lamp was irradiated in air through a photomask where a test pattern is figured. The irradiated part can be resolved with water due to the main chain scission, resulting in the decrease in the molecular weight, which is confirmed by GPC measurement. As a result, the fine positive pattern was efficiently produced after development with water (35 °C). The microscope photograph indicates that the fine patterns based on the line-and-space with a resolution of 0.75 μm, which is the highest resolution of the photomask employed in this study, can be clearly drawn with no swelling (Fig. 6).

LB film thickness of the exposed portion as a function of exposure time was measured to estimate the sensitivity as

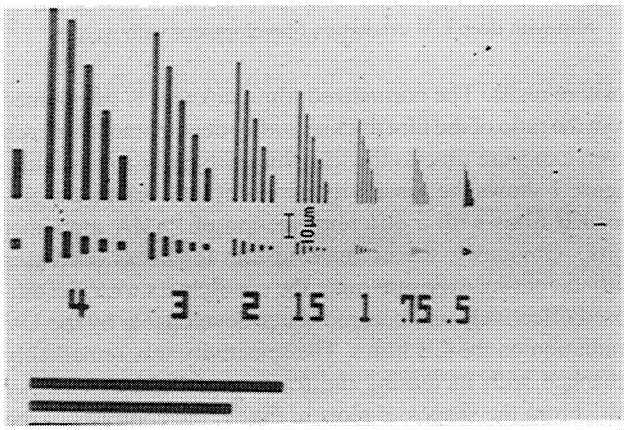


Fig. 6. Optical micrograph of positive fine patterns with COP30 LB film (70 layers) on a silicon wafer after deep UV irradiation and being developed in water.

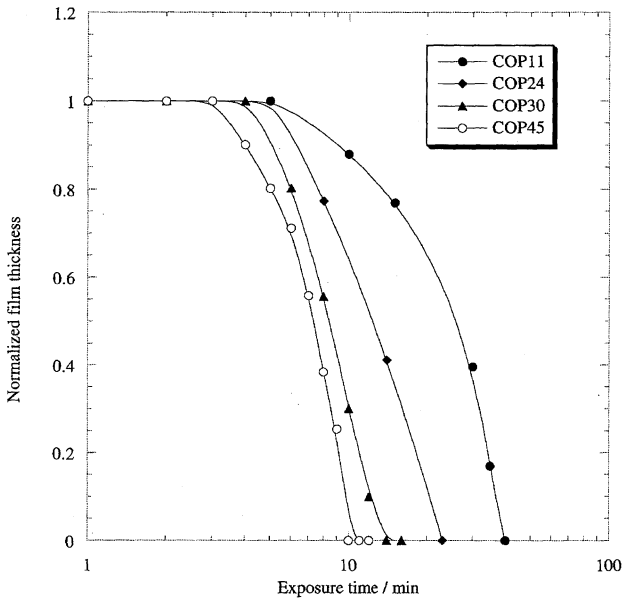


Fig. 7. Sensitivity curves of the copolymer LB films with various copolymer compositions for deep UV irradiation.

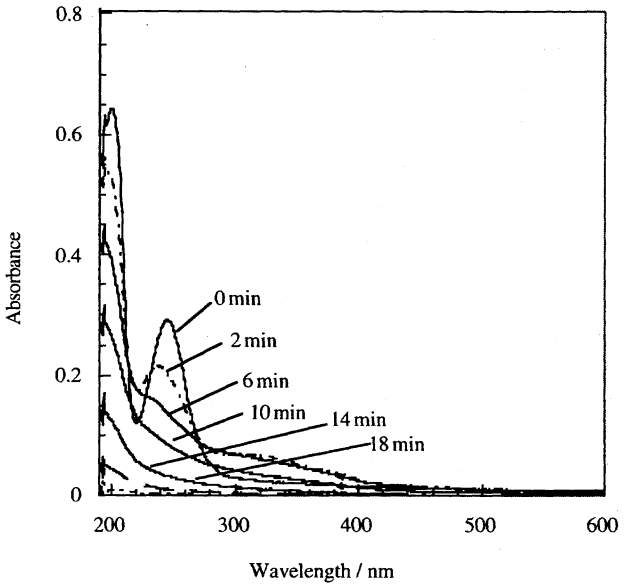


Fig. 8. Change of the UV absorption spectra of COP30 LB film with deep UV irradiation (development with water).

positive resist. The normalized film thickness is determined from the ratio of the film thickness after development for each given exposure time to the film thickness prior to exposure. Figure 7 shows the sensitivity curves of the various copolymer LB films with a different fraction of PhMA monomer units. Obviously, the normalized film thickness decreases with increasing exposure time; the copolymers were decomposed effectively and became water-developable by the UV irradiation on the LB films. The sensitivity was remarkably enhanced with increasing the fraction of PhMA monomer unit. From the shapes of plots in Fig. 7, the contrasts of the LB films were obtained to be 3.6 (COP11), 2.2 (COP24), 3.3 (COP30), and 4.5 (COP45), respectively.

Figure 8 shows the change of UV-visible spectra of COP30 LB film (80 layers) with deep UV irradiation. The absorbance around 245 nm decreases with irradiation time. Apparently, on irradiation, the LB film undergoes photodegradation of the polymer backbone and bond scission of side chain. Studies of the detailed mechanism of the decomposition reaction and of further lithographic properties are now under way.

Thus, a water-developable positive photoresist system using the poly (DMA-co-PhMA) LB films has been developed. Deep UV irradiation with a high-pressure Hg lamp on the copolymer LB film produced a positive fine pattern with high resolution of 0.75 μm after developing in warm water. The sensitivities of the copolymer LB films were remarkably enhanced with increasing mole fraction of PhMA monomer unit.

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