Preparation of a New Photodegradable Copolymer LB Film and Its Application to Photopatterning

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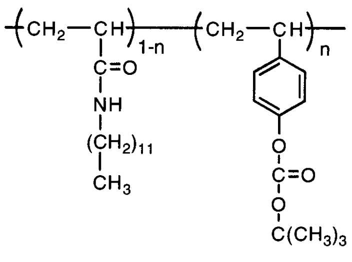
A new type of copolymer LB film containing a photodegradable monomer, *tert*-butyl 4-vinylphenyl carbonate (*t*BVPC), was prepared. It was found that the p(DDA/*t*BVPC) LB film could be efficiently decomposed by deep UV irradiation. After development with an alkali solution a positive-tone pattern could be drawn with a high resolution of 0.75 μm.

Langmuir-Blodgett (LB) technique makes it possible to prepare an ultra-thin film with controlled thickness and well-defined molecular orientation at a molecular size,[1,2] while molecules are randomly distributed in polymer spin-coated films. Because of this superior feature, polymer LB films have been investigated for the application to high-resolution lithographic technology with deep UV, electron beam, and X-ray beam in order to construct the state-of-art nanostructure on solid substrates with development process to remove the exposed portion (positive type) or the unexposed portion (negative type).[3,4]

In the previous studies,[5-8] we have found that stable uniform polymer LB films can be fabricated from a polyalkylacrylamide structure. Furthermore, we succeeded in producing fine patterns by the polymerization of alkylacrylamide monomer LB films, in addition, by the cross-linking reaction in polymer LB films with deep UV and electron beam irradiation. All of these LB films resulted in the negative-tone photopatterns. On the other hand, we also obtained a positive type photopatterning using poly(*N*-tetradecylmethacrylamide) LB film without any development process (dry-development).[9,10]

In the current article, we will describe the formation of a new type of polymer LB film capable of drawing a positive photopatterning. The polymer ((p(DDA/*t*BVPC)) was prepared by free-radical polymerization of *N*-dodecylacrylamide (DDA) and *tert*-butyl 4-vinylphenyl carbonate (*t*BVPC) in dry toluene at 60 °C with AIBN as a thermal initiator. The second comonomer could be incorporated in the LB films up to ca. 50 mol%. The copolymer was purified by reprecipitation in acetonitrile. The molar ratio of the *t*BVPC in the copolymers was determined by measuring ^{1}H NMR spectra.



p(DDA/*t*BVPC)

First, the monolayer property of p(DDA/*t*BVPC) on the water surface was investigated by the measurement of surface pressure (π) and area (A) isotherms. A chloroform solution of the copolymer was spread on the water surface ($>$ 17.0 MΩ cm). The π-A isotherm of p(DDA/*t*BVPC53) (the content of *t*BVPC is 53 mol%) shows a steep rise in pressure and a high collapse pressure (Figure 1), indicating the formation of the condensed monolayer on the water surface. The average surface limiting area per repeating unit can be obtained from the extrapolation of the linear part of the isotherm to zero surface pressure. Moreover, the surface area for the *t*BVPC monomer is estimated to be approximately 0.48 nm^2 / monomer, assuming that the surface area of DDA group is 0.28 nm^2 / monomer.[11] This means that the benzene ring and the *tert*-butoxycarbonyloxy (*t*-BOC) group are oriented vertically to the water surface. The copolymer monolayer can be transferred onto a solid support with both downward and upward strokes at 20 mN m^{-1} and a dipping speed of 10 mm min^{-1}. The transfer ratios were almost unity, showing the formation of Y-type LB films. The UV absorption spectra of the multilayer films of p(DDA/*t*BVPC53) on a quartz are shown in Figure 2. The p(DDA/*t*BVPC) LB films have maxium absorbance at 193 nm. The inset shows clearly a linear relationship between the absorbance at 193 nm and the number of layers, which indicates that the regular deposition of the monolayer onto the solid substrate occurs.

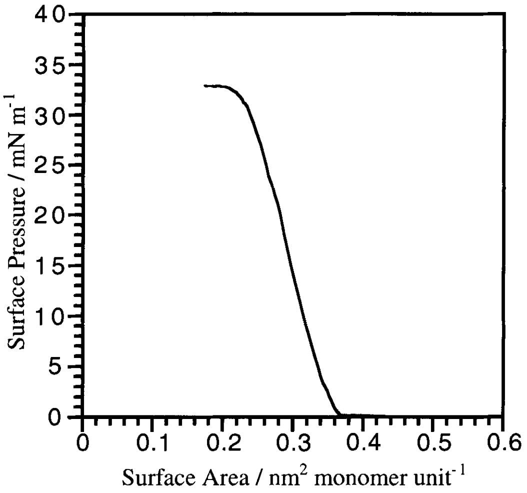


Figure 1. Surface pressure and area isotherm for p(DDA/tBVPC53) at 15 °C.

The LB film of p(DDA/*t*BVPC53) with 40 layers was directly exposed to deep UV light through a photomask in air

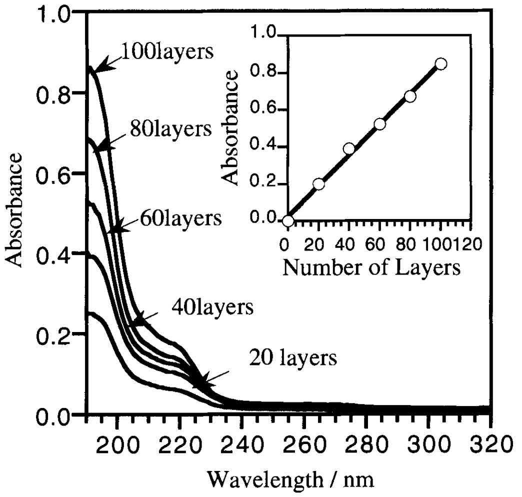


Figure 2. Absorption spectra of p(DDA/tBVPC53) LB films as a function of number of deposited layers.

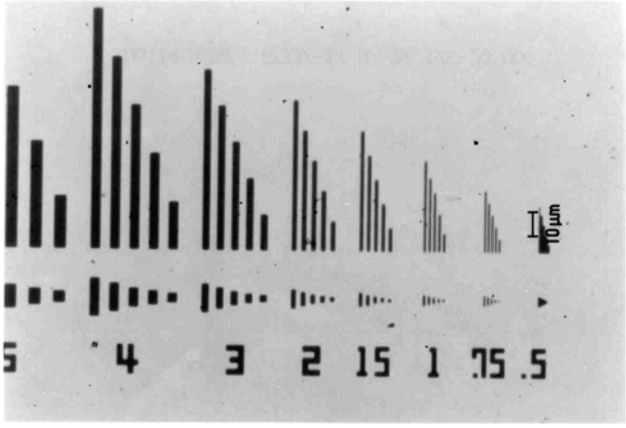
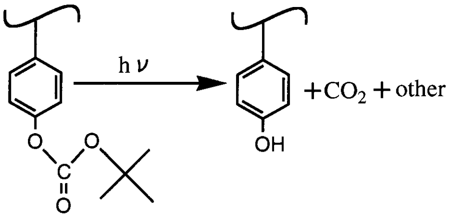


Figure 3. Optical micrograph of 0.75 μm positive patterns of p(DDA/*t*BVPC53) LB film with 40 layers on a silicon wafer.

atmosphere for 40 min, followed by development with 10 wt% tetramethylammonium hydroxide (TMAH) aqueous solution. A fine pattern with a line width of 0.75 μm was drawn (Figure 3). It is of interest that the positive photopatterns could be drawn with p(DDA/*t*BVPC53) LB film, while the homopolymer pDDA LB film gave negative photopatterns with deep UV irradiation after the development in toluene.[10] The positive patterning results from the fragmentation of *t*-BOC group caused by deep UV irradiation, which leads to the formation of phenolic resin capable of being dissolved in aqueous-base developer (Scheme 1).[13]

Scheme 1.



In conclusion, a new photodegradable copolymer, p(DDA/*t*BVPC) was prepared. The copolymer can form the stable and condensed monolayer on the water surface and be transferred onto solid substrates such as quartz, glass, and silicon slide, giving Y-type uniform copolymer LB films. Deep UV irradiation on p(DDA/*t*BVPC) LB film was carried out. After the development with TMAH aqueous solution, the positive fine pattern could be drawn with a high resolution of 0.75 μm. The present result suggests that the copolymer LB film containing *t*-BOC group has a high potential application to a new type positive-tone resist such as chemically amplified or top surface imaging resists.[14]

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