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Micropatterning of Schiff Bases Polymer Langmuir-Blodgett (LB) Films

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Abstract. A series of novel copolymers poly (AOBDA-co-DNMMA)s containing 2-Allyloxy-N-benzyl- idene dodecylamine (AOBDA) and 1.4-dioxaspiro[4.4] nonane-2-methyl methacrylate (DNMMA) were synthesized. The copolymers could form stable condensed monolayer at air/water interface and be transformed onto solid substrates successively. Positive-tone patterns with the resolution of 0.75 μm of the copolymers Langmuir-Blodgett (LB) films with 40 layers were obtained by deep UV irradiation, followed by developing in acetone. The etched gold patterns with resolution of 0.75 μm were also obtained, showing that the copolymer has enough resistance to wet etching suitable for fabricating photomask. The mechanism of photolysis was also investigated by UV, IR and GPC.

Introduction

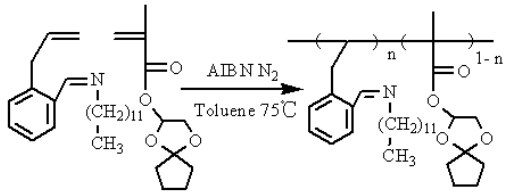
Schiff bases are one of the important classes of organic compounds and have extensive applications in biological function materials, ultraviolet stabilizers and laser dyes as well as molecular switches in logic or memory circuits. So far, two important properties of Schiff bases are widely involved, especially for those Schiff bases from salicylaldehyde. Trans/cis isomerization, photochromism and some organized molecular films of these photochromic derivatives are reported. As a ligand, Schiff bases could coordinate with various metal ions [1-3]. The photo chromic properties of Schiff bases are closely related to the intra molecular hydrogen bonding, while the coordinative properties intensely depend on the coordination of the imine and hydroxyl groups with the metal ions. But, research on Schiff bases from salicylaldehyde as amphiphile for LB films technology applied to photolithography has seldom been reported.

Langmuir-Blodgett (LB) technique makes it possible to prepare a thin film with a controlled thickness at the molecular level with a well-defined molecular orientation. Resists using LB films for high-resolution lithographic technology have been widely investigated for this excellent feature. In previous studies [4-6], we found that stable uniform polymer LB films can be fabricated from a polyalkylacrylamide. Fine patterns *via* polymerization of alkylacrylamide through a cross-linking reaction in polymer LB films could be drawn under deep UV and electron beam irradiation (negative-tone). We also obtained a new type of positive pattern without using any development process (self-development) and with aqueous alkali [7-13]. Combining LB films with blending photoacid generators (PAG) into polymer LB films directly and PAG introduced in polymer backbone and with the heterodeposited LB films, which made it much more versatile than the systems obtained with a conventional method was also studied[14-16]. In the present paper, a series of novel copolymers p(AOBDA-co-DNMMA)s containing 2-Allyloxy-N-benzylidene dodecylamine (AOBDA) as film formation material and 1,4-dioxaspiro[4.4] nonane-2-methyl methacrylate (DNMMA) were synthesized and their monolayer, photopatterning and photodecomposition mechanism were investigated.

Experimental section

Synthesis of copolymer p(2-Allyloxy-N-benzylidene dodecylamine-co-1.4-dio-xaspiro[4.4]-nonane-2-methyl methacrylate) p(AOBDA-co-DNMMA)s

Copolymers p(AOBDA-co-DNMMA) (shown in Fig.1) was prepared by free radical polymerization with different AOBDA ratio in toluene at 60 ºC using AIBN as initiator under nitrogen for about 24 h. The copolymer was precipitated three times into a large amount of methanol. The precipitates were filtered and dried under vacuum at room temperature. Various polymer solutions in chloroform (0.5 mg/ml) were prepared, and then filtrated over 0.22 μm filters. The copolymers compositions were determined by ^{1}H NMR spectra. The properties of the copolymers are summarized in Table 1.



AOBDA DNMMA p(AOBDA-co-DNMMA)

Fig. 1 Chemical structure of p (AOBDA-co-DNMMA)s

Table 1 Date of p(AOBDA-co-DNMMA)s

Polymer	AOBDA(mol%) in feed	(in real*)	Yield (%)	Mn (X 10^4)	Mw (X 10^4)	Mn /Mw
3a	50	(53.4)	40.1	1.32	1.66	1.25
3b	60	(50.9)	76.5	1.67	2.16	2.16
3c	70	(60.0)	20.3	1.50	2.68	1.79
3d	80	(79.2)	36.7	1.33	1.89	1.42

* Measured with ^{1}H NMR

Measurements

^{1}H NMR, UV and IR were measured with NMR DPX-400 (Bruker, German) in $CDCl_3$, Lambda 35 UV-Visible spectrometer (Perkin Elmer Inc. USA) and Bruker Vector-22 FT-IR spectrometer. Deep UV irradiation was carried out with EX250 UV light source (Honya-Schott Ltd, Japan). Molecular weight was measured with gel permeation chromatography GPC50 (PL) using polystyrene as standard. Patterns were observed by microscope (OLYMPUS BX51, OLYMPUS Co. Japan). Measurement of surface pressure (π) - area (A) isotherms and the deposition of monolayer were carried out with a computer controlled Langmuir trough system (KSV-5000-3, KSV Instruments, Helsinki, Finland). Gold film was prepared by BTT-IV system (Bench Top Turbo IV Coating System).

Results and Discussion

Monolayer behaviour at the air/water interface and film formation

The copolymers p(AOBDA-co-DNMMA)s were spread on the water surface at 20 ºC to measure surface pressure (π) - area (A) isotherms shown in Fig. 2. The isotherms showed a sharp rise in surface pressure and a high collapse pressure, indicating the formation of condensed monolayer on the water surface. Among of these curves the **3a** could help to obtain higher collapse pressure above 55 mN/m.

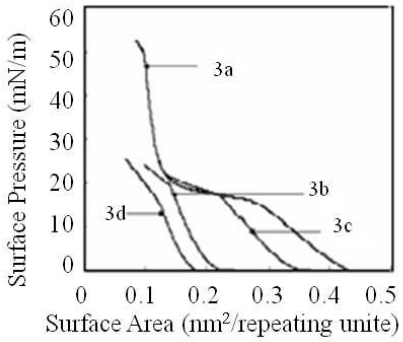


Fig. 2 π-A isotherms of p(AOBDA-co-DNMMA)s at 20 °C

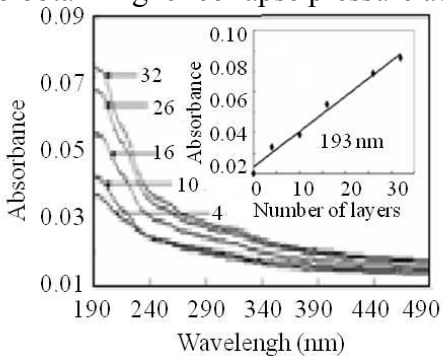


Fig.3 UV absorption spectra of the **3a** LB films as a function of the number of layers deposited. Inset: Plots of the absorbance at 193 nm as a function of the number of layers deposited.

The UV spectra of copolymer **3a** LB films (deposited under 30 mN/m) were measured as a function of the number of layers deposited (Fig.3). The intensity of maximal absorbance at 193 nm was proportional to the number of layers, indicating that copolymers **3a** monolayer could be transferred onto substrate (Fig.3 Inset). The monolayer of copolymers **3b, 3c** and **3d** also could be transferred onto solid substrate as a Z-type LB films under a given surface pressure with a regular transfer ratio.

Photopatterning

The copolymer **3a** LB films with 40 layers was directly exposed to the deep UV light through a photomask in the air for 40 min, followed by developed in acetone for 2s. As shown in Fig.4, we obtained a clear pattern with a resolution of 0.75 μm, which is the resolution limit of the photomask employed in the present work. Therefore, the subsequent experiments for photopatterning were carried out with **3a** LB films.

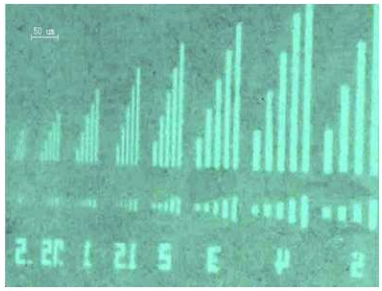


Fig. 4 Optical micrograph of 40 layers **3a** LB films on silicon irradiated by deep UV, following developed in acetone.

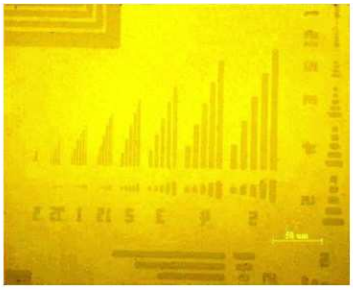


Fig. 5 Optical micrograph of etched gold film pattern on glass substrate

Etching properties

The copolymer **3a** LB films with 40 layers were deposited on the gold film which was sputtered on glass substrate and were irradiated though a photomask for 40 min. Then positive-tone patterns of LB films were obtained after developing in acetone for 2s. The patterns were immersed into a mixed solution composed of iodide (0.6g), ammonium iodide (1.5g), ethanol (20ml), and water (30ml) for 20s, and then was wished with chloroform to remove the residual copolymer **3a** LB films. Finally, the etched gold patterns with the resolution of 0.75μm were obtained (Fig.5). It indicated that a 40-layer **3a** LB films provided good resistance to the wet etchant.

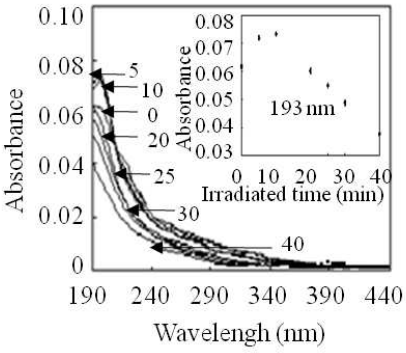


Fig.6 UV spectra of copolymer **3a** LB films irradiated by deep UV. Inset: relationship between the irradiated time and the maximal absorbance at 193 nm

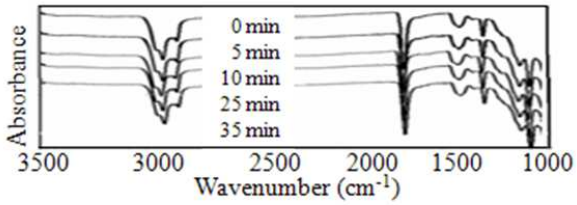


Fig.7 IR spectra of 2b LB films deposited on CaF_2 irradiated by deep UV for 0, 5, 15, 25 and 35 min.

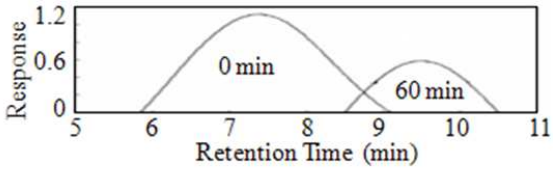


Fig.8 G PC of 3a before and after irradiation

Photodecomposition mechanism of copolymer LB films

Figure 6 showed the change of UV spectra of **3a** LB films exposed to deep UV light (λ=250 nm) without photomask. The absorbance band at 193 nm was decreased, indicating **3a** LB films were sensitive to deep UV light. These features of **3a** LB films suggested that the scission of main or side chain decomposition occurred. Figure 7 showed the change of FT-IR spectra of **3a** LB films which were deposited on CaF_2 substrate irradiated by deep UV light for different time-interval. Absorbance

at approximately 3476 cm^{-1} in the IR spectra of the LB films, assigned to the stretching vibration of hydroxyl group, was increased and broadened after irradiation, which is the evidence that the hydroxyl group was produced by the irradiation [17]. Moreover, The peaks at 1107 cm^{-1} assigned to the stretching vibration of C-O-C disappeared as well as the band at 1730 cm^{-1}, 2922 cm^{-1} and 1625 cm^{-1} which is assigned to the carbonyl group, alkyl group and C=N group weakened, which means that 1.4-dioxaspiro [4.4] nonane ring group is removed from the side chain to give a carboxylic group that can be dissolved in acetone or water. These changes could confirm the scission of side chain in the copolymer LB films. The photolysis mechanism was also studied by gel permeation chromatography (GPC) measurement. The GPC measurement was carried out in order to confirm the molecular weight change during the deep UV irradiation. Because the amount of the LB films was too small, the measurement had to carry out with spin-coating film. Figure 8 showed the number average molecular weight of **3a** before and after (60 min) irradiation (λ=250nm). The decrease of number average molecular weight after irradiation indicated that scission of main chain of the copolymer took place.

Conclusions

A series of novel copolymers p(AOBDA-co-DNMMA)s containing AOBDA as film formation material in the polymer unit and DNMMA as photosensitive group were synthesized. They could form condensed monolayer at the air/water interface and be transferred to solid substrate. Copolymer **3a** LB films were successfully applied to photopatterning and yielded fine patterns with the resolution of 0.75μm. It was also demonstrated that the copolymer **3a** LB films have sufficient resistance to a wet etching process. The formation of the pattern was attributed to the scission of the main chain and the cleavage of the side chain in LB films. The photo patterning properties of p (AOBDA-co-DNMMA) LB films are expected to be applied as a photoresist.

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