

Studies on photolithography and photoreaction of copolymer containing naphthyl in ultrathin nanosheets induced by deep UV irradiation

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Abstract

A novel polymer containing photoactive naphthyl group, poly (*N*-dodecylmethacrylamine/ β -naphthylmethacrylate) (pDDMA-NPMA) was synthesized and its molecular arrangement and photochemical reactions were investigated in ultrathin film. The polymer p (DDMA-NPMA) could self-aggregate into a crystal film at air/water interface and this monolayer could be transferred onto solid supports, giving Y-type uniform Langmuir-Blodgett (L-B) films. Upon deep UV irradiation, photochemical reaction occurred in L-B films, and the irradiated parts could be eliminated as the verified images of optic-microscopy, resulting in a fine positive tone photolithographic patterns with a resolution of 0.75 μm . Changes of molecular chemistry induced by the 248 nm light treatment were investigated by atomic force microscopy, fluorescence, ultraviolet, Fourier transform infrared spectroscopy and gel permeation chromatography (GPC). The results showed that the main route of the photoreaction was dimerization of the naphthylene, and then photodecomposition of not only naphthyl group but also main chains of polymer. In the present paper, several possible mechanisms of photochemical reaction induced by deep UV light were also proposed.

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1. Introduction

The generation of images through photo-induced chemical changes in sensitive coatings remains a fertile field for fundamental and applied research. In fact, the prospect of fabricating even smaller and faster microelectronic and microoptoelectronic devices has driven the research of new microlithographic resists of even higher resolution, sensitivity and endurance. So far, relief images for new microlithography with submicron resolution and excellent process latitude have been achieved

by combining advanced technology with new chemistry [1]. The increased solubility in the exposed areas can be caused by decomposition of resist by various lithographic techniques such as deep UV light, vacuum UV, electron beam, and X-rays to realize a high resist resolution [2–5]. Deep UV lithography is one of the most promising technologies for sub-0.5 μm features delineation [6], because it has many economic and technical advantages over previous technology [7]. Ordered super-molecular assembly based on functional molecules and photochemical reaction has been attracting considerable interest for the application to molecular devices and DNA chips [8,9]. Langmuir-Blodgett (L-B) techniques is one of the most effective ways in preparing nano-assembled ultrathin films at a molecular level with high molecular orientation on solid substrate [10]. Since the photochemical reactions usually depend on the orientation of the molecules, Langmuir monolayer at

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air/water interface and the L-B films on solid substrate can serve as good modes to investigate photochemical reaction [11,12].

Photochemical proportion of photoresist is very important for photolithography. Ito et al. have made a systematic examination of the resist called chemically amplified resists (CARs) [13], which are sensitive to acid. Many investigations are focused on the ultraviolet (UV) irradiation of photoresists containing 2-trimethylsilyl, ketal, *tert*-butylcarboxylate or a cross-linkable group in the main chain resulting in the photodecomposition or photopolymerization [6,14,15]. Miyashita's group has been successful in the preparation of a preformed polymer L-B films containing a cross-linking group [4,10], resulting into a fine negative pattern consisting of two-dimerization network by cross-linking at deep UV light and EB irradiation and producing positive-tone photopatterns using poly (*N*-tetradecyl methacrylamide) L-B films without any development process (self-development) [16,17]. However, all of these researches are concerned with syntheses of a novel class of chemically amplified photoresists and evaluates of the resist's structure, resolution and sensitivity.

Photo-oxidative decomposition of polymer such as PMMA has been described in detail in some literatures [19–23], but there is limited information about the behavior of ultrathin film, especially nanosheet film. Comparing with huge amounts of investigations on the kind and property of photoresist, fewer are devoted to the chemical reaction mechanism introduced by irradiation. Particularly, there are few reports on the photochemical reaction in the monolayers and super-molecular assembly nanosheets.

Naphthalene, a typical aromatic hydrocarbon, is a widely investigated photoactive compound and its photoreaction in organized media has been widely investigated [24,25]. In our previous studies, we have devised, synthesized and prepared novel copolymer L-B films of *N*-dodecylmethacrylamide (DDMA) with β -naphthyl methacrylate (NPMA). We found these copolymers could form stable monolayer and could be transferred successfully onto solid substrate. On deep UV irradiation, a fine positive-tone pattern with higher sensitivity and a resolution of 0.75 μm , which is the highest resolution of the photomask employed in this study, was obtained without any development process (self-development) (Fig. 4). These photochemical properties induced by deep UV in nanosheet films have attracted our considerable interest from fundamental and application viewpoints. In this paper, a novel kind of photoresist containing naphthalene moiety was synthesized and the molecular assembly and photoreaction in L-B films have been investigated.

2. Experimental

2.1. Synthesis

N-dodecylmethacrylamide (DDMA) was synthesized from α -methacryloyl chloride with dodecylamine in the presence of triethylamine and chloroform at 0 °C. The crude prod-

Table 1

Molecular characteristics of pDDMA-NPMA before and after deep UV irradiation

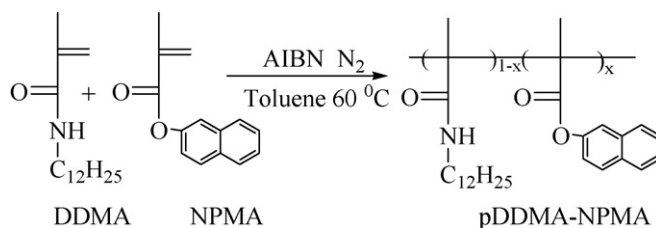
Irradiation time (min)	M_n (10^{-3})	M_w (10^{-3})	M_w/M_n	S^a
0	28.39	52.28	1.84	–
60	3.77	4.74	1.26	6.54
180	1.63	5.79	3.55	16.38

^a The number of chain scission per initial polymer molecule.

uct was purified by column chromatography (100–200 mesh of gel, eluted: acetic ether/petroleum ether = 1/5). A colorless crystalloid was obtained after the solution was removed and dried under vacuum overnight. The yield was 83%, m.p. 37–38 °C. The ¹H NMR data was given as follows: (CDCl₃ ppm) δ 0.86–0.90 (t, 3H), 1.26–1.30 (d, 18H), 1.49–1.57 (q, 2H), 1.96 (s, 3H), 3.28–3.33 (q, 2H), 5.30–5.31 (d, 1H), 5.66 (s, 1H), 5.80 (s, 1H). FT-IR (cm⁻¹): 3330–3050 ($\nu_{\text{N-H}}$), 1653 ($\nu_{\text{C=O}}$), 1607 ($\nu_{\text{C=C}}$), 1534 ($\delta_{\text{N-H}}$), 1473 ($\nu_{\text{C-N}}$). Element analysis: cal. C % 75.83; H % 12.37; N % 5.53; found: C % 75.32; H % 12.45; N % 5.34.

β -naphthyl methacrylate (NPMA) was synthesized from α -methacryloyl chloride with β -naphthol in the presence of triethylamine and chloroform at 0 °C. After 2 h, the reaction mixture was washed twice with NaHCO₃ and NaCl aqueous solution, respectively. Then the organic layer, which was dried with anhydrous MgSO₄ overnight, was filtrated and concentrated to give the white solid. The crude product was purified by column chromatography (100–200 mesh of gel, eluted: acetic ether/chloroform/petroleum ether = 1/1/30). A colorless crystalloid was obtained after the solution was removed and dried under vacuum overnight. The yield was 81%, m.p. 69–70 °C. The ¹H NMR data was given as follows: (CDCl₃ ppm) δ 1.92 (s, 3H), 5.51 (s, 1H), 6.05 (s, 1H), 6.98–7.70 (m, 7H). FT-IR (cm⁻¹): 3085 ($\nu_{\text{C-H}}$), 1745 ($\nu_{\text{C=O}}$ of ester), 1640 ($\nu_{\text{C=C}}$ of naphthalene), 1310, 1100 ($\nu_{\text{C-O-C}}$ of ether).

Poly (*N*-dodecylmethacrylamide-co-naphthylmethacrylate), p (DDMA-NPMA) was prepared by free-radical copolymerization in toluene at 60 °C, 2, 2'-azobis isobutyronitrile (AIBN) as a thermal initiator. The molecular weight (M_w , M_n) and molecular weight distribution (M_w/M_n) of the copolymer (the NPMA content was 50 mol% in feed), which were obtained by gel permeation chromatography (PL GPC 50, Polymer Lab, UK) using a polystyrene standard, are shown in Table 1, respectively. The reaction steps are described in Scheme 1. In the same way, poly (naphthylmethacrylate) (pNPMA)



Scheme 1. Polymerization of pDDMA-NPMA.

and poly (*N*-dodecylmethacrylamide) (pDDMA) were also obtained.

2.2. Monolayer characterization

The experiments for monolayer spreading on water were performed on a Langmuir-Blodgett system (KSV-5000-3, KSV Instruments, Helsinki, Finland) equipped with computer controls. A Wilhelmy plate was used as the surface pressure sensor and was situated in the middle of the trough. Two barriers compressed or expanded symmetrically at the same rate from two sides of the trough. Distilled and deionized water with resistant values higher than 18.2 M Ω cm (MILI-Q gradient, MILIPORE CO., USA) was used for a subphase. The copolymer was dissolved in chloroform at a concentration of approximately 0.5 mg/ml and the solution was spread on the water surface by a micrometer syringe. After spreading, we waited for about 30 min to let the solvent evaporate out; the monolayer compression started at a compression rate of 10 mm/min. The subphase temperature was controlled by water circulation from a thermostat within an error range of ± 0.5 °C. The isotherms for every sample were measured twice to ensure good reproducibility.

2.3. Fabrication of polymer Langmuir-Blodgett films

Polymer L-B films were fabricated onto quartz, silicon, mica and gold-covered glass substrates by the vertical dipping technique at a surface pressure of 25 mN/m and a dipping speed of 5 mm/min. The substrate surface was set to be perpendicular to the moving direction of the barrier. In the course of deposition, after each cycle of the downward and upward stroke, the substrate was kept dry in air for 10 min, so that the following monolayer could be transferred favorably. The forward (backward) speed of the barrier was set to be 5 mm/min.

2.4. Characterization of polymer L-B films

UV-visible and fluorescence spectrum were obtained with Lambda 35 UV-Visible (Perkin-Elmer Inc. USA) and FluoroMax-P (Jobin Yvon Inc. USA) spectrophotometer, respectively. Atomic force microscopy (AFM) observation was carried out on SPM-9500 J3 (Shimadzu corporation, Japan) under a phase imaging mode in the air condition of 20 °C. Both height and phase image were recorded simultaneously using the retrace signal. IR spectrum was measured with Infrared spectrometer (Bruker VECTOR, German). ^1H NMR was measured with NMR DPX-400 (Bruker, German). Deep UV irradiation was carried out with EX250 UV light source (Honya-Schott Ltd., Japan). Photopatterning was observed by microscope (OLYMPUS BX51, OLYMPUS Co., Japan). Gel permeation chromatography was made on PL GPC 50 (Polymer Lab, UK). Polymer solution in tetrahydrofuran (1% w/v) was prepared, and then filtrated over 0.2 μm filters.

3. Results and discussions

3.1. Polymer monolayer at the air/water interface and L-B film formation

The copolymer pDDMA-NPMA and homopolymer pDDMA were spread on water surface from a chloroform solution to measure surface pressure (π)-area (A) isotherm of monolayer. The $\pi - A$ isotherm of pDDMA-NPMA showed a steep rise in the surface pressure with a high collapse pressure about 50 mN/m, suggesting the formation of a stable condensed monolayer (Fig. 1). The limiting molecular area per repeating unit occupied by the pDDMA-NPMA was estimated to be 0.52 nm 2 from the extrapolation of the linear part of the isotherm to zero surface pressure. The value was smaller than the summation of homopolymer pDDMA (0.36 nm 2) and pNPMA (0.44 nm 2 , not shown in Fig. 1). This implied that multilayer or a two-dimensional (2D) crystal film might form at that time. In order to confirm this deduction, monolayer of the spreading film was transferred on silicon wafer and its AFM image was studied, as shown in Fig. 2A. Numerous fangs and clusters of fangs were observed in the pDDMA-NPMA film, while the surface of pDDMA was very flat (Fig. 2B). This indicated that strong interactions between the hydrophobic naphthyl groups caused multilayer or crystal formation of pDDMA-NPMA. The analogous multilayer formation or crystallization on water surface was reported previously [24,25,27]. The pDDMA-NPMA monolayer could be transferred onto quartz and silicon wafers as a Y-type film. Fig. 3 shows UV absorption spectra of the deposited pDDMA-NPMA L-B film as a function of the number of layers. In comparison, the corresponding spectrums in methanol solution were also shown (dotted line). In methanol solution, the absorption peaks appeared at 221 and 275 nm; they were typical absorption of naphthyl group and could be assigned to E $_1$ and E $_2$ transition bands, respectively. However, both of the two bands in L-B films showed a red shift compared with those in methanol solution (the E $_1$ shifted to 228 nm, while the E $_2$ to 280 nm), which indicated that the naphthyl group aggregates in L-B films were a head to tail arrangement [25]. The inset in

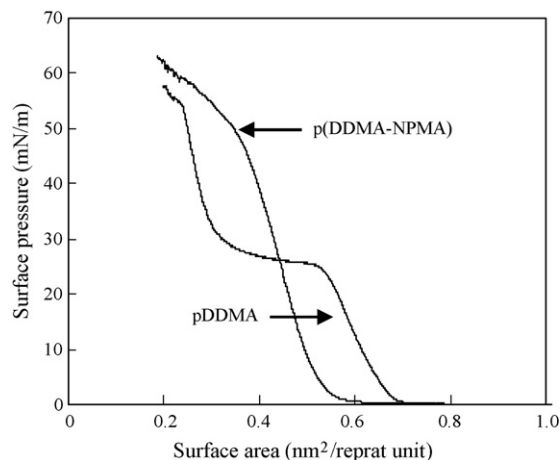


Fig. 1. Surface pressure-area isotherms of pDDMA-NPMA and pDDMA on the water surface at 25 °C with a compression rate of 10 mm/min.

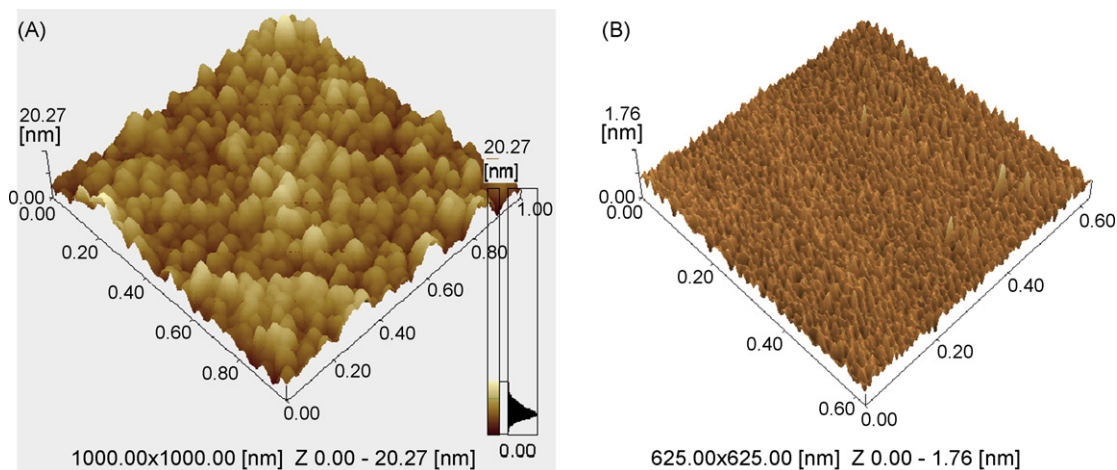


Fig. 2. Topographic images of monolayer L-B film of copolymer pDDMA-NPMA on silicon (A) and homopolymer pDDMA (B) on mica.

Fig. 3 shows that the absorbance at 228 nm apparently increased in a linear mode at a higher rate up to 11 layers, and then at a lower rate for more layers, which indicated that a few copolymer monolayer could be deposited on the substrate. This behavior implied that the regular deposition of the copolymer monolayer occurred fewer than 11 layers.

3.2. Photodecomposition image

Naphthyl group is photoactive and can dimerize upon photoirradiation with UV light [24]. Such kind of photoreaction on the L-B film was investigated through observation of the morphological change of the ultrathin film as a function of irradiation time. Fig. 4A shows the optical micrograph of pDDMA-NPMA L-B films of 11 layers irradiated with a deep UV light source (248 nm) for 5 min through a photomask. Fig. 4B and C are the photolithography process schemes of the square region marked in Fig. 4A, where the barrier image represented the exposed areas and the masked regions, respectively. We could

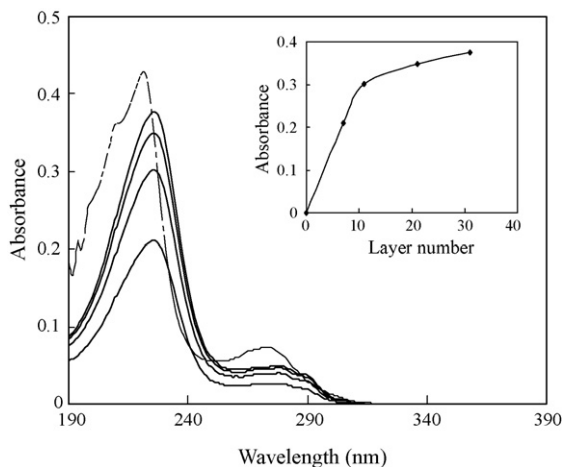


Fig. 3. UV absorption of pDDMA-NPMA L-B films as a function of deposited layers. Dotted line is the UV absorbance spectra of pDDMA-NPMA in methanol solution. Inset: plots of the absorbance at 228 nm vs. the number of L-B films deposited.

distinctly see that the exposed areas were much brighter than the masked regions; viz. the thickness of pDDMA-NPMA L-B films in the irradiated region became much thinner than that in no-irradiated region. So, the brightness changes indicated that the photochemical reaction could occur in the L-B films and the reaction brought out the photodecomposition of pDDMA-NPMA. The microscopic photography showed that fine patterns could be drawn at the maximum resolution of $0.75 \mu\text{m}$ line-and-space, which was the highest resolution of the photomask employed in this study. In addition, the process of photoreaction could be further confirmed by AFM. The monolayer of pDDMA-NPMA was transferred on silicon substrate at surface pressure 25 mN/m by an up stroke movement and irradiated directly with a 248 nm UV light for 0, 1, 11, and 21 min, and

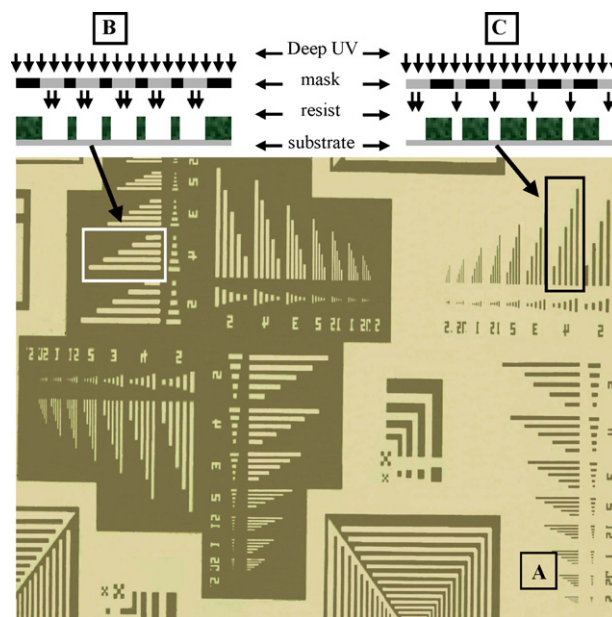


Fig. 4. (A) Optical micrograph of pDDMA-NPMA L-B films with 13 layers on a silicon plate irradiated with a deep UV light for 5 min. (B) The square region marked in (A) (where the barrier image represented the exposed area). (C) The square region marked in (A) (where the barrier image represented the masked area).

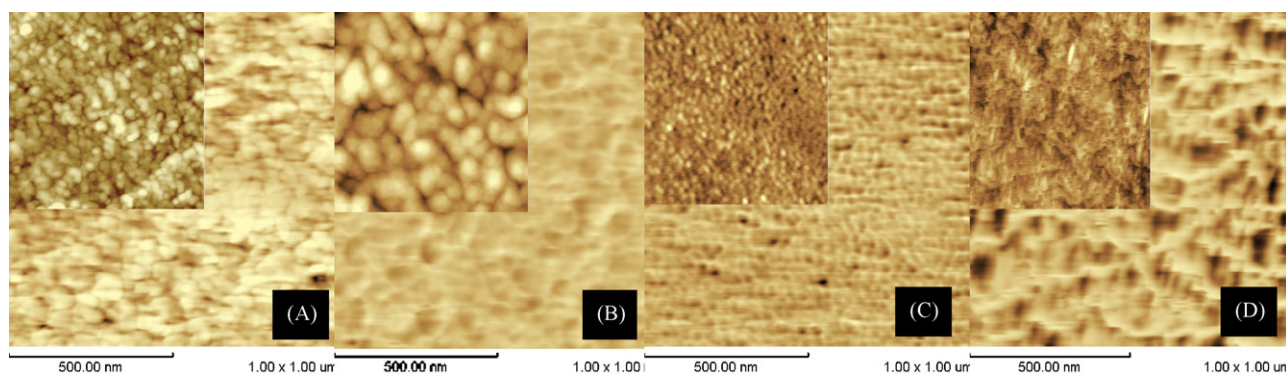


Fig. 5. AFM images ($1.00 \times 1.00 \mu\text{m}$) of pDDMA-NPMA L-B films on silicon showing the variation of the morphology with irradiation: (A) 0 min; (B) 1 min; (C) 11 min; and (D) 21 min. Inserted: the high images.

the collected AFM images are shown in Fig. 5 A–D, respectively. Fig. 5A shows an image of the monolayer L-B film without irradiation, in which numerous fangs were observed and it was due to the aggregation of molecular on the water surface. The film had the rough surface (roughness was 1.463 nm) and large mean particle radius ($0.028 \mu\text{m}$). With further irradiation on the surface, the particle diminished to be mean particle radius of $0.009 \mu\text{m}$ and the film became more homogeneous and smooth with the roughness about 0.9 nm (Fig. 5C). It was also found that many holes with irregular shapes appeared randomly on the flat film surface, as seen in Fig. 5C. As irradiation continued, the particle reduced in size and merged into homogeneous phase where no particle character could be found (Fig. 5D). The number and the size of holes grew with the exposure time, in the end, and the film surface became rougher. Meanwhile, the film thickness got much thinner after photo-irradiation, which was in accordance with the optical image changes in multilayer films shown in Fig. 4. It was interesting that the particle irradiated for 1 min grew double and quintupling in size comparing with those irradiated for 0 min and 11 min (shown in Table 2); it indicated that the photo-aggregation could also happen at that time. Therefore, we thought that the photochemical reaction, not only photodecomposition but also photo-aggregation, could occur in the L-B films during deep UV irradiation.

3.3. UV-vis and fluorescence spectra

The dramatic changes in the UV-vis absorption spectra of pDDMA-NPMA and pNPMA L-B films of 13 layers deposited on quartz substrate are shown in Fig. 6A and B, respectively. On deep UV irradiation, the absorption of naphthyl

moiety (at 228 and 280 nm) dropped dramatically and almost disappeared within 15 min, as showed in the insets of Fig. 6A and B. There were almost no changes in the UV spectra upon further irradiation.

It was interesting to note that upon deep UV irradiation, absorption band at 228 nm disappeared significantly and a new band appeared at 196 nm. After irradiation for 4 min, the UV peak at 196 nm reached the max, and then decreased rapidly. In order to interpret the nature of the new band, we had measured the UV-vis spectra of the L-B films of homopolymer pNPMA (Fig. 6B). The similar phenomenon was also found in the case of pNPMA L-B films. It was suggested that naphthyl group could undergo topochemical photodimerization at the initial stage of irradiation (Scheme 2 pathways1), viz. naphthyl changed into phenyl and small molecule became macromolecule, resulting in the change of the peak from 228 to 196 nm and the UV absorption at 196 nm increased rapidly. On further irradiation, photodecomposition became main factor and the naphthyl-dimers broke away from the main chain of polymer, so the absorption at 196 nm dropped rapidly. It was worth noting that the absorption at 196 nm was the blue shift band of the typical phenyl moiety at 205 nm. Because the blue shift corresponded to the H-aggregation of the chromophores [25] and the mean radius of particle in L-B film irradiated for 1 min grew double compared with that for 0 min (shown in Table 2 and Fig. 5B), it was suggested that arrangement change of naphthyl group in L-B films took place from J-aggregation to H-aggregation, and then the photo-dimerization.

Further evidence of the photochemical reaction of naphthyl chromophore was from the fluorescence spectra at $\lambda_{\text{exc}} = 278 \text{ nm}$, as shown in Fig. 7. The emission bands from the copolymer (Fig. 7A) and the homopolymer (Fig. 7B) decreased markedly and a new band at 430 nm appear clearly in Fig. 7B upon deep UV irradiation. The broad emission band was assigned to the emission from the dimer of the naphthyl group [24]. The appearance of the new band revealed the process of the photodimerization in the p(DDMA-NPMA) L-B films. It should be noted that there was a less conspicuous change at 430 nm in the fluorescence spectra of copolymer than homopolymer (Fig. 7A and B). This could be due to the few topochemical photodimerization products, and the photodegradation happened rapidly at same time.

Table 2
The particle analysis of pDDMA-NPMA monolayer L-B film before and after deep UV irradiation

Irradiation time (min)	Roughness (nm)	Partical area (10^3 nm^2)	Mean radius ($10^2 \mu\text{m}$)
0	1.46	3.00	2.80
1	1.47	6.00	4.30
11	0.90	0.35	0.90

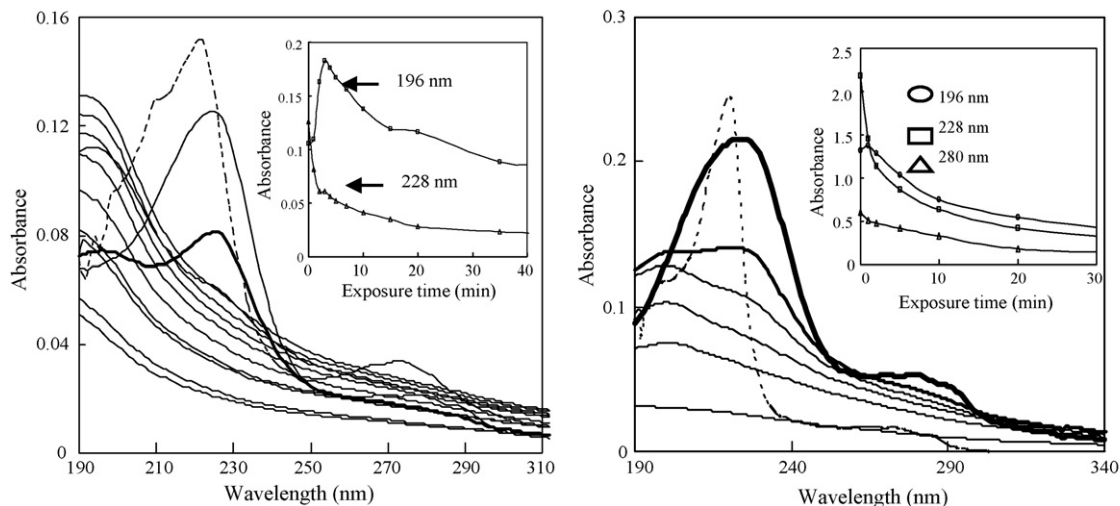


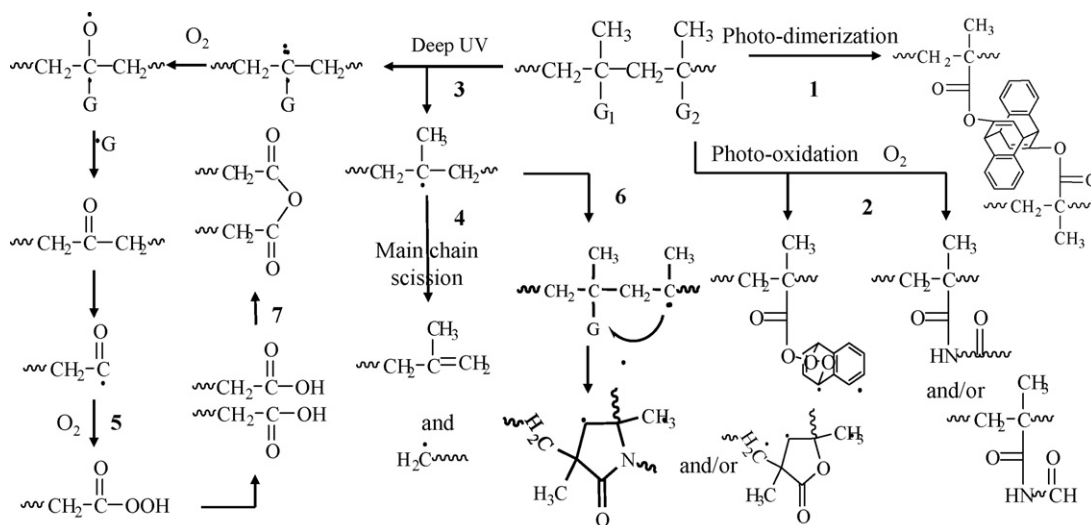
Fig. 6. UV absorbance spectra of pDDMA-NPMA L-B film with 13 layers (A) and pNPMA film (B) before (bold line) and after 1, 2, 3, 4, 5, 7, 10, 15, 20, 35, and 45 min of deep UV irradiation. Dotted line is the UV absorbance spectra in methanol solution. Inset: relationship between absorbance and irradiation time at 196, 228 and 280 nm.

3.4. FT-IR spectra

Photochemical reaction (photodimerization and photooxidation) in p (DDMA-NPMA) L-B films deposited on CaF_2 substrate was detected by FTIR. Significant changes caused by deep UV irradiation were observed practically in the IR region as shown in Fig. 8.

The destruction of the naphthalene unit was confirmed by the disappearance of a weak band at 1620 cm^{-1} in the spectrum of the irradiated copolymer. It was the characteristic frequency for a skeletal in-plane vibration of the naphthalene ring. Meanwhile, a new absorption at 1580 cm^{-1} appeared rapidly upon irradiation, which was assigned to the C=C vibration of benzene-like structure. Thus, it was clear that the naphthalene was transformed into a substituted product of photodimeriza-

tion and/or photooxidation in copolymer irradiated at ambient air (as Scheme 2 pathway 1 and 2 shown). Photo-oxidation decomposition occurred in the pDDMA-NPMA L-B films was revealed by IR spectra. Oxidation structures appeared in the copolymer molecules soon after 1 min irradiation treatment: The new broad absorption bands appeared at $3500\text{--}3800\text{ cm}^{-1}$ and were responsible for free (non-associated) and hydrogen bonded hydroxyl/hydroperoxide group, which could not be distinguished; the carbonyl peak broadened at 1720 cm^{-1} and at lower wavenumbers. With irradiation time increasing, spectra changes were more extensive. The general and progressive decrease of the principal polymer peaks reflects the volatilization of small molecules, in agreement with the change of molecular weight (as shown in Table 1). The destruction reaction was observed on the basis of absorbance change at $2850\text{--}2950\text{ cm}^{-1}$.



G = N-dodecylacetamide and naphthalen-2-ly acetate

G₁, G₂ = N-dodecylacetamide and naphthalen-2-ly acetate, respectively.

Scheme 2. Several possible photodecomposition and photochemical pathways induced by deep UV at ambient air.

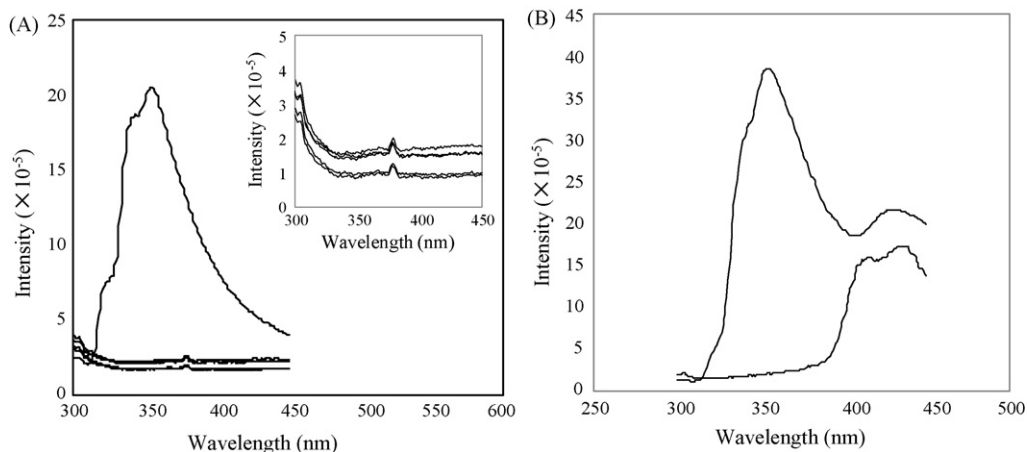


Fig. 7. Fluorescence emission spectra of the L-B films of (A) pDDMA-NPMA and (B) pNPMA deposited on silicon before (upper curve) and after deep UV-irradiation (lower curves) ($\lambda_{\text{exc}} = 278 \text{ nm}$) at ambient air.

The bands were assigned to the following methyl and methylene group vibrations: ν_s ($\text{CH}_3\text{-O}$), ν_a (CH_3), ν_s (CH_3) and ν_s (CH_2), where ν_a was asymmetric stretching, ν_s was symmetric stretching. The fast decrease of methyl/methylene groups in the polymer during exposure to deep UV was not only to degradation of side groups and backbone structure abstraction but also to oxidation. Polymeric oxidation products underwent further photolysis and volatile low molecular weight products can be evolved according to the mechanism proposed (pathways 3 and 4 in Scheme 2).

The other feature of oxidation during irradiation was the gradual increase of new absorption which extended up to 1830 cm^{-1} and reached maximum at 1790 cm^{-1} . The oxidative decomposition of pDDMA-NPMA upon deep UV initiated through reaction of oxygen molecules with the radicals formed probably by abstraction of the hydrogen atoms of the structure units, followed β -scission and formation of ketones or aldehyde at 1720 cm^{-1} [19] as shown in pathway 3. At the same time, acid groups which had absorption at 1700 cm^{-1} might be also formed at this stage, as shown in pathway 5. The growing of the broad absorption between 1830 and 1790 cm^{-1} could partially be attributed to the formation of γ -lactim and/or lactone structures (as shown in pathway 6) which were ubiquitous in all types of aliphatic polymers photodecomposition [19], but mainly to the formation of open chain anhydride whose main

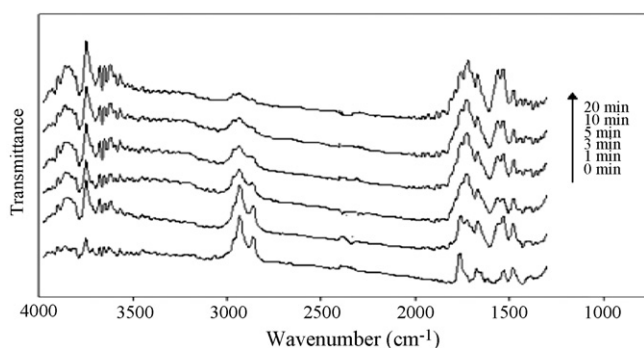


Fig. 8. FTIR transform spectrum of pDDMA-NPMA after 0, 1, 3, 5, 10 and 20 min of deep UV-irradiation at ambient air.

absorption was around 1800 cm^{-1} , such structures might be generated according to the reactions of pathway 7.

3.5. Gel permeation chromatography results

In order to reveal the mechanism of the photo-induced decomposition or photolysis, the changes of the molecular weight of the polymer before and after of deep UV treatment were investigated by gel permeation chromatography (GPC), the results were listed in Table 1. The change curves in molecular weight distribution (MWD) are shown in Fig. 9. The number average molecular weight (M_n) decreased and the molecular weight distribution became broader during the irradiation; it indicated that the random scission of copolymer chain took place.

From the number average molecular weight, the number (S) of chain scission per initial polymer molecule was obtained through the relationship [26].

$$S = \left[\frac{M_n}{M_n} \right] - 1$$

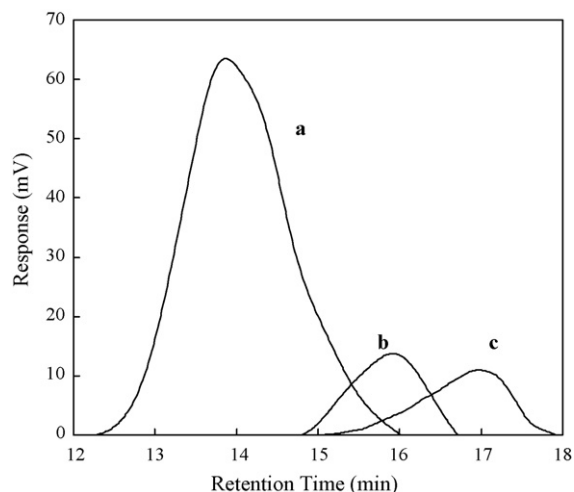


Fig. 9. GPC curves of pDDMA-NPMA before (A) and after deep UV-irradiation for 60 min (B) and 180 min (C).

Where, $M_{n(0)}$ and $M_{n(t)}$ are the number average molecular weight of polymer before and after t min of deep UV irradiation, respectively. It was seen that the numbers of chain scission were very high after 60 and 180 min irradiation (Table 1). It indicated that pDDMA-NPMA was very sensitive for deep UV irradiation; maybe it easily underwent decomposition or depolymerization. The samples exhibited significant increase of polydispersity (M_w/M_n) after deep UV irradiation; it meant copolymer molecules became more non-uniform. We also noted that at the initial irradiation period, the number of chain scissions increased at a higher rate until 60 min than at a lower rate. This behavior implied that chain scissions occurred randomly in the two different kinetic regimes along the polymer molecules.

4. Conclusions

Copolymer, pDMMA-NPMA could aggregate into crystal film in water surface and was transferred on solid substrate to form ultrathin film by Langmuir-Blodgett technique. It was found that the copolymer had high sensitivity to deep UV irradiation. The exposed parts in L-B films could be eliminated as verified the images of optic-microscopy, as a result, a fine positive tone photolithographic patterns with a resolution of 0.75 μm was figured without any development process. Some photochemical reactions induced by the 248 nm light treatment could occur and were investigated by atomic force microscopy, fluorescence, ultraviolet, Fourier transform infrared spectroscopy and gel permeation chromatography. The results showed that a topochemical reaction (photodimerization) of naphthyl chromospheres occurred in the copolymer L-B films at the initial stage of irradiation, which was special, and then a decomposition reaction of polymer. Moreover, according to the growth of the number of chain scission per initial polymer molecule and the decrease of molecular weight after irradiation, the mechanism of photo-oxidative decomposition could be expanded: Oxidation could take place not only in the main chain but also in the side groups. Several probable mechanisms of photochemical reaction induced by deep UV light were also proposed.

Just for the high sensitivity to deep UV irradiation, pDMMA/NPMA, which has a structure subjected to decomposition in main chain scission and side chain cleavage, can be used in the dry-development photo-resist system and we also expect that the copolymer is applicable to fabrication of nano-filter and nano-tube.

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