

Effect of C=C content on the film properties of electrodeposition photoresist

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Abstract

A photosensitive amphiphilic random copolymer (UPDHES) was prepared by modifying the acrylic random copolymer, poly (*N*, *N*-domethyl amimethyl methartylate-*co*-2-hydroxypropyl methacrylate-*co*-2-ethylhexyl acrylate-*co*-styrene) (PDHES) precursor. Self-assembling of random copolymer UPDHES into photosensitive micelles in water, followed by the orientated deposition of UPDHES micelles in the electric field, ultimately produces photoresist film. The curing kinetics of the photoresist film for different C=C content had been investigated during the curing process. The effects of different C=C content were studied by evaluating various properties of the film such as the MEK resistance, hardness, thermal stability, dynamic mechanical analysis and tensile strength test. Moreover, the photoimaging properties of the electrodeposition photoresist with different C=C content were studied by resolution test.

Keywords: UV curing; Self-assembling; Photoresist; Electrodeposition

1. Introduction

In terms of global PCB structure, the next generation electronic system requirements for the PCB prominently shown in aspects such as high-density, multi-functional, miniaturization and lightweight, in the meanwhile, multilayer board, flexible printed circuit board, flex-rigid board, HDI/BUM board, IC packaging base board were in high demands these years. To date, three photoresist coating techniques have been introduced for the fabrication of MEMS devices. Spin coating is the most conventional coating method, generally applied to standard flat wafers^[1]. It can only be used for some MEMS applications with certain modifications of the equipment or spinning method used or of the coating program. Alternative methods such as electroplating and spray coating^[2, 3] of photoresist have been proposed. At the same time, with the development of the PCB, conventional photoresist such as dry film and liquid photoresist could not meet the requirements of the higher resolution. So far as multilayer PCB (external line width 0.10-0.12 mm, internal line width 0.10 mm, spacing 0.075 mm) used for Ball Grid Array Package (BGA) is concerned, the pattern transformation would not obtain its technological indexes using above processes.

Electrodeposition process easily forms a uniform film as compared with the conventional coating techniques, it processes high throwing power which is the ability to deposit a uniform film on a complex-shaped surface. The electrodeposition film also has

excellent resistance to corrosion [4]. Electrodeposition of photoresist [5, 6] has been reported as an attractive method for 3D stacks of chips and interconnects. The main advantage of this electrodeposition photoresist is the conformal resist layer independently of the geometry of the nonplanar features. The most critical part to be coated like the obtuse top corner and concave bottom corner of the cavities are covered by a layer of the same thickness as on the surface of the copper foil. Electrodeposition photoresist is the most suited technique to pattern structures that run in and across cavities or when a smaller line width is required.

In this study, the preparation of commercially available photosensitive UPDHES micelles is reported. The photoresist film was produced by electrodeposition of UPDHES micelles, and then preceded to exposure-development procedure. The effects of different C=C content of UPDHES were studied by investigate the chemical, mechanical and thermal properties, and resolution test.

2. Experimental

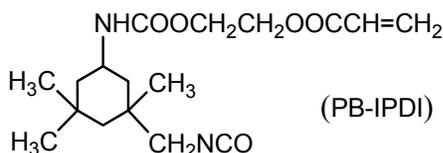
2.1. Preparation of UPDHES micelles

In this work, a photosensitive amphiphilic random copolymer (UPDHES) was prepared by modifying the cationic acrylic random copolymer (PDHES) with PB-IPDI (Scheme1), the ¹H NMR spectrum of UPDHES is shown in Fig 1. As a result the C=C content of UPDHES is controllable. The C=C content was calculated according to the following formula:

$$C = 1000 \times M_{C=C} / m$$

Where *C* is the C=C content, *M_{C=C}* is the mole number of the monomers containing C=C and *m* is the total mass of the photosensitive copolymer^[7].

In a typical experiment, to the UPDHES was dissolved in Ethyl acetate in a round-bottom flask. To the solution was then added lactic acid and photoinitiator (Irgacure 1173), and the reaction mixture was stirred for 30 min. The photosensitive random copolymer UPDHES micelles were formed by the addition of the random copolymer UPDHES solution into water at a constant rate with continuous stirring. The UPDHES micelles solution was stirred for 24 h.



Scheme 1

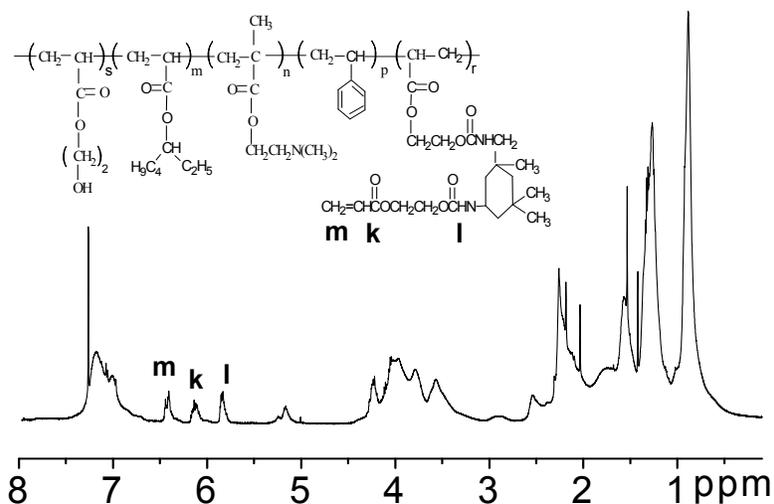


Figure.1 ^1H NMR spectrum of photosensitive random copolymer

2.2. Electrodeposition process of UPDHES micelles

Photoresist films were prepared on copper foil by electrodeposition process. Copper foil, serving as cathode, was immersed into the UPDHES micelles solution under constant dc voltage and time. The cathode-to-anode distance was 10 cm. After a 5min flash-off process at 70 °C, transparent photoresist film was obtained.

2.3. UV irradiation of films

UV curing of photoresist samples was performed using a medium-pressure mercury lamp in air; light intensity was 325 mW/cm².

2.4. Measurement

The ^1H NMR data were obtained from a Bruker AVANCE DRX500 spectrometer at 25 °C;

The particle size of UPDHES micelles was measured by ALV-5000/E Dynamic Laser Light Scattering with measurement size ranging from 0.001 to 5 um diameter;

The morphology of micelles was investigated by transmission electron microscopy (Philips CM120 microscope), operating at an acceleration voltage of 80 kV;

Photoinfrared experiments were performed using a Nicolet5700 with detector type MTC KBr, The light source was a medium-pressure mercury lamp (EFOSLite 50 W). Such setup monitors the reactive functional group conversion as the photo reaction proceeds and is known as real-time infrared spectrometry (RTIR). Photoresist samples were spin coated onto a KBr plate, which were then exposed to UV light. Scans were taken over a 180 s period at 54 scans/min. The UV intensity was adjusted to 40 mW/cm² and the experiment was performed in air. The C=C conversion was monitored at 810 cm⁻¹;

Hardness testing was performed with a Gardener pendulum hardness tester (QBY-2 , Senrida Co., China) on glass substrate;

Methyl ethyl ketone (MEK) double rub experiment was used to assess the solvent resistance of the cured photoresist films. After 100 double rubs the cloth was rewet with MEK. The number of double rubs was reported as the point where mar appeared on the film surface was recorded.

Tensile property was measured by LRXPLUS (Lloyd) at 25 °C. All measurements had an average of five runs. The dumbbell type specimen was 25mm wide at two ends and 6mm wide at the neck, film thickness was measured using a micrometer. The thermal analysis was measured by TGA-209 (Netzsch) at temperatures from 25 to 700 °C and 20 °C /min heating rate in N₂ atmosphere.

Dynamic mechanical thermal analysis (DMTA) was accomplished using a Instruments 242 DMA (Netzsch). The sample size for testing was 12mm×6 mm and film thickness was measured using a micrometer. The analysis was carried out from -60 to 100 °C at a frequency of 1Hz and a ramp rate of 3 °C/min.

Resolution of the photoresist was determined by examining the developed circuit diagram under microscope. The exposure-development procedure was as follows:

- The negative-type photoresist was uniformly spread on a copper foil substrate by electrodeposition process, and then prebaked at 70 °C for 5 min.
- Following UV irradiation under a photomask at 430 mJ/cm² (UV source: broadband, 235–400 nm, Blue Sky Co., China), it was developed with a developer liquid for 30 s, HAc/H₂O=1/49.
- Then using optical microscope DZ-4 (Union) to examine the resolution.

3. Results and discussions

3.1. The particle size distribution and morphology of UPDHES micelles

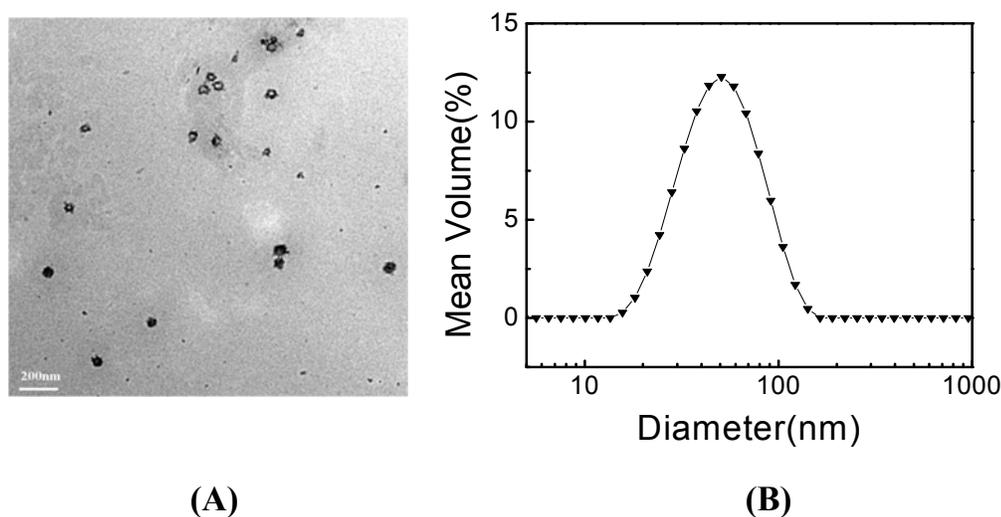


Fig.2 The particle size distribution and morphology of UPDHES micelles
(DMAEMA content =10.29%, Neutralization degree =90%)

The UPDHES micelles were prepared by the self-assembly of photosensitive random copolymer UPDHES. UPDHES micelles were formed by first dissolving random copolymer UPDHES in good solvent (ethyl acetate) and then gradually adding water as a nonsolvent for hydrophobic segment.

The TEM images of the micelles prepared in selective solvents are shown in Figure 2A. The random copolymer UPDHES formed mainly a regular sphere-shaped aggregate. The diameters of the spheres were in the range of 30-90 nm. This observation was reasonable because the formation

process of micelles was a dynamic process of mechanical balance, with the addition of poor solvent H₂O, the hydrophobic segments gathered because of hydrophobic interaction, and the hydrophilic segments quickly moved to the interface of aggregates and H₂O by the hydrophilic interaction. A similar phenomenon was also observed in the other micelle system^[8,9].

The average size and size distribution of UPDHES micelles could also be determined from dynamic laser light-scattering (DLS) measurement. The R_h was 51 nm for sphere-shaped micelles (Figure 2B) from the DLS method, which was consistent with the TEM results. The hydrodynamic radius distribution of the micelles was unimodal, also indicating formation of the expected monodispersed nano-scale micelles.

3.2. The effect of C=C content on the conversion of C=C Bond

The effect of the C=C content on the curing behavior of photoresist films was studied. Fig.3 shows the RTIR spectra of curing system at different irradiation time. The conversion rate was calculated according to following formula:

$$DC (\%) = 100 \times (A_0 - A_t) / A_0$$

A_0 , A_t was the peak area of =CH at 810cm⁻¹ after 0 and t seconds irradiation respectively.

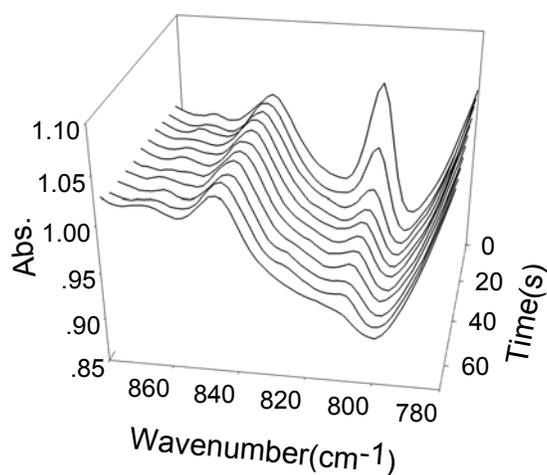


Fig.3. RTIR spectra of curing system at different irradiation time

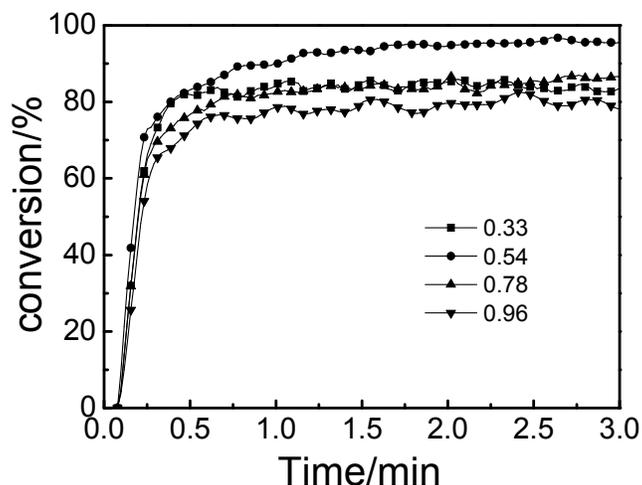


Fig.4. Effect of C=C content on the conversion of C=C
 ($I = 40 \text{ mW/cm}^2$, [photoinitiator] = 3%)

Fig. 4 shows the relationship between the C=C conversion for different C=C content samples and the radiation time. It can be seen that the conversion of C=C bond was low when C=C content is higher. The sample with 0.33 meq/g C=C content showed the final conversion reach to 87% and the sample with 0.54 meq/g C=C content showed the highest final conversion reach to 97%. This trend can be understood by taking into consideration the influence of chain mobility. The conversion rate, that was the cross-linking rate of C=C bond, which showed a restriction of molecular chain motion ability. At the same conversion rate, the sample with higher C=C content had higher cross-linking density, it will reach to lower final conversion ratio because of the restriction of the chain movement.

3.3. The MEK resistance and the pendulum hardness of the film

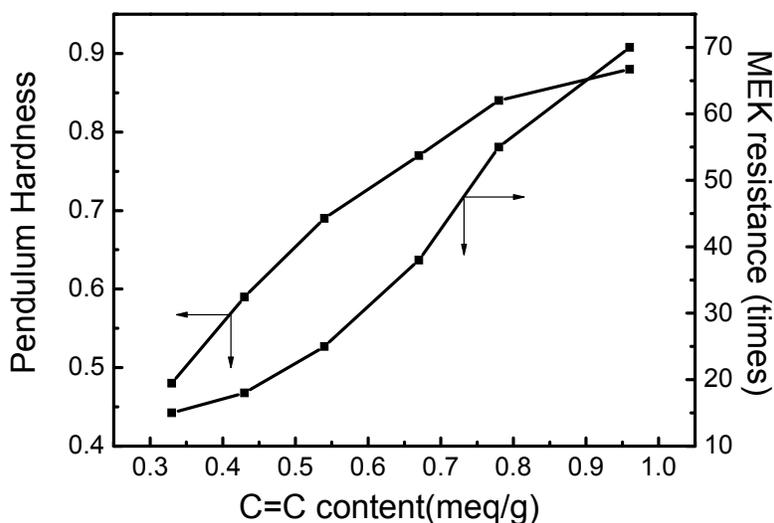


Fig.5. The correlation of the MEK resistance and Hardness to the double bond content

In order to improve the MEK resistance and the pendulum hardness of the photoresist films, the cross-linking density of the film should be improved. In this work we use the PB-IPDI to introduce the C=C bond into the side of the structure of the amphiphilic random copolymer UPDHES, therefore the C=C content was controllable and higher C=C content was obtained. Fig. 5 shows the correlation between the MEK resistance and the pendulum hardness to the C=C content. From the figure, it can be understood that when the cross-linking density of the UV cured film was raised, the MEK resistance and pendulum hardness of the cured film were improved consequently. When the C=C content was 0.33 meq/g, the scrub times just 15 times. For the sample with C=C content of 23.04 meq/g the scrub times can reach to about 70 times. The results presented that a better MEK resistance and Hardness of photoresist film need for additional multi-functional reactive diluent.

3.4. The thermal analysis of the film

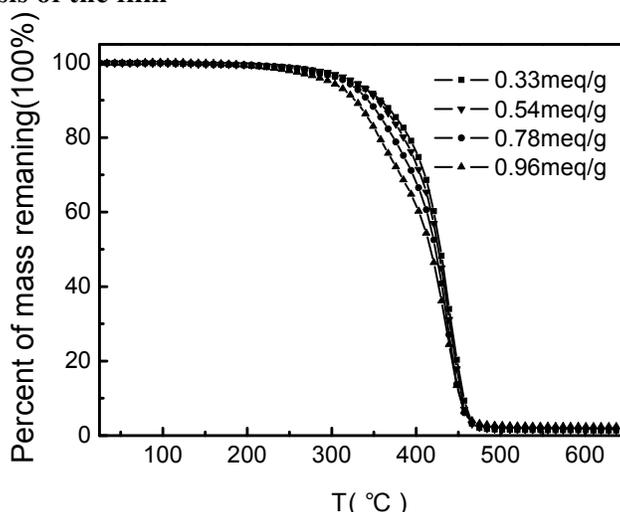


Fig.6. The thermogravimetric curves of the cured films

Thermogravimetric analysis (TGA) showed that the thermal stability of the cured photoresist film with the different C=C content as shown in Fig. 6. Generally, the higher of the C=C content, the better was the thermal stability of the film. For the samples with higher C=C content the cross-linking density of the films were higher, which lead to the better thermal stability of the films.

But from the figure, the thermal stability of the cured photoresist film was decreased with the increasing of C=C content. The initial decomposition temperature was 195 °C for the sample with 0.96 meq/g C=C content. In addition, it was found that the TGA curve had the similar final resolution ratio for the samples with different C=C content.

It can be understood that the thermal dissociation of blocked isocyanates bond^[10]. In this work, C=C bond was introduced by half-blocked isocyanates (PB-IPDI), sample with higher C=C content had more blocked isocyanates bond will result in the decrease of initial decomposition temperature. The samples with different C=C content had the similar final resolution ratio, because the thermal dissociation of blocked isocyanates bond lead to the destruction of cross-linking network and they had the same main-chain structures acrylic random copolymer PDHES.

3.5. The Dynamic Mechanical thermal Analysis of the film

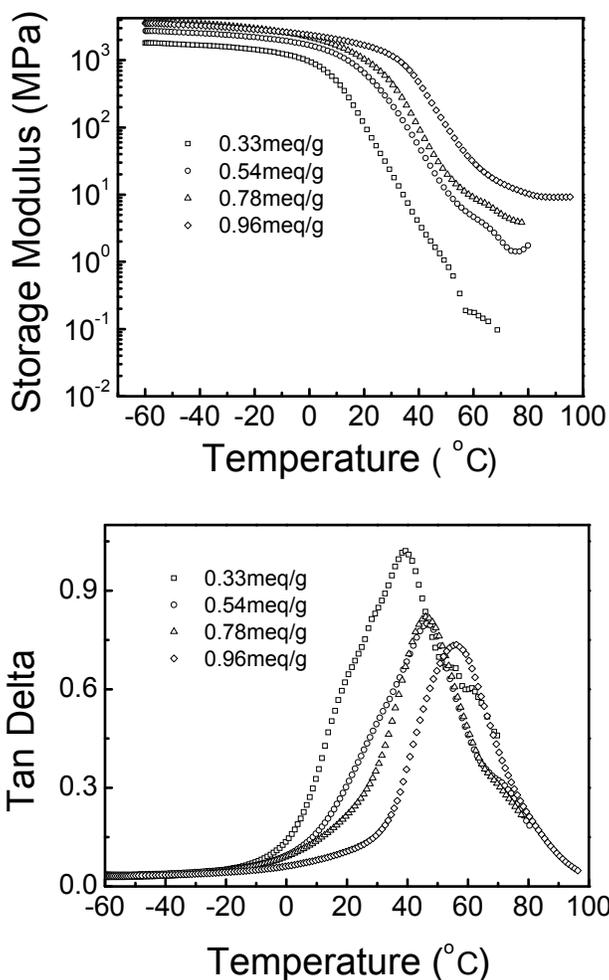


Fig.7. DMA spectra of the UV cured films formed with different double bond content

The dynamic mechanical thermal analysis (DMTA) is a common technique to examine the viscoelastic behavior of polymer systems, including the glass transition behavior. DMTA tests were performed for the UV-cured films with different C=C content. The influence of C=C content on the storage modulus and $\tan \delta$ of the films cured under UV is shown in Fig. 7. The increased of C=C content of photoresist film caused a corresponding increase in storage modulus owing to higher cross-linking density of the resin system.

Fig. 7 also shows the plots of loss factor ($\tan \delta$) versus temperature. The glass transition temperature (T_g) of a cross-linking material can be determined as the relaxation peak of the $\tan \delta$. The T_g follows the similar trends with the storage modulus. The samples with 0.54 meq/g and 0.78 meq/g C=C content had the same T_g . There were mainly two competitive factors which affect the T_g of the cross-linking network. On the one hand, the increased in T_g was attributable to enhanced cross-linking network of sample with higher C=C content. On the other hand, the higher C=C content of sample, the more urethane unit contained in the structure of photosensitive copolymer, increased of urethane unit content will result in the decrease of the T_g of the cross-linking network.

3.6. The tensile properties of the film

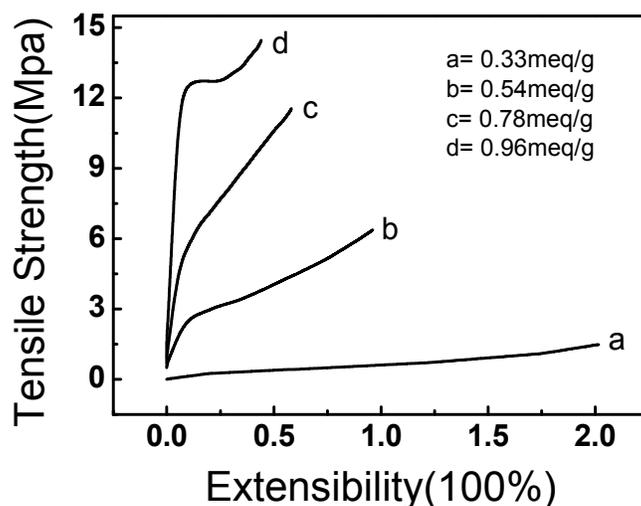


Fig.8. Effect of double bond content on tensile strength of UV cured films

Fig. 8 shows the stress–strain curves of the cured photoresist films. As the increasing of the C=C content, the tensile strength and the initial modulus increased accordingly, but the extensibility of the films reduced. When the C=C content was higher (e.g. 0.96 meq/g) the film showed a brittle trend and had lower extensibility. With the reduction of the C=C content, the films presented a yielding trend with the increasing of the corresponding extensibility and the reduction of the tensile strength and the initial modulus. For the sample with C=C content of 0.33 meq/g the extensibility can exceeded 200%. These tensile properties proposed that C=C bond plays an important role in increasing the strength and extensibility of the photoresist films, and the UPDHES photoresist films had the excellent extensibility especially for the future application in flexible printed circuit board.

3.7. Resolution test

Finally, it was important to know how high the resolution the electrodeposition photoresist can achieve after a standard exposure–development process, in case that industrial application was targeted. Fig. 9 shows the optical microscopic images of the developed photoresists with different C=C content. The cured photoresist films with 0.33 meq/g and 0.54 meq/g C=C content were dissolved in development process because of low cross-linking density. From figure.9, the resolution of sample with 0.96 meq/g was better than sample with 0.78 meq/g. It can be understood that electrodeposition photoresist with higher C=C content had higher resolution owing to higher cross-linking density. Figure.9B shows a microscopy image of a prepared photoresist. The width of the line was about 15 μm , and the edge of the line was relatively flat and free of roughness. The result proposed that the photoresist had a resolution meeting the industrial requirement.

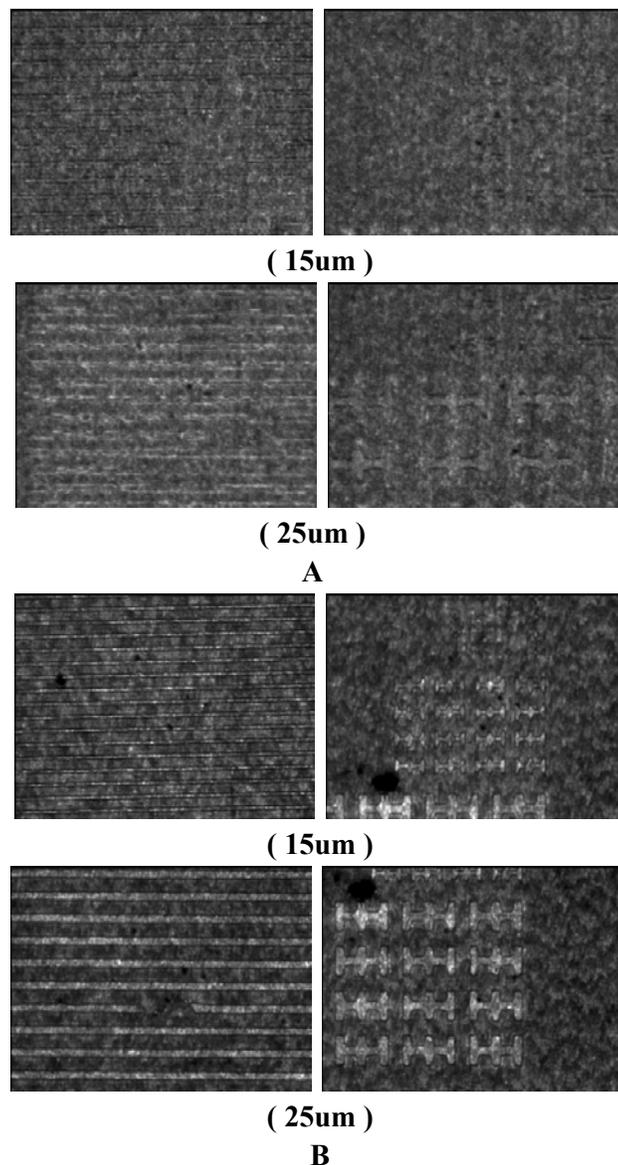


Fig.9. Optical microscopic image ($\times 350$) of the patterns formed using electrodeposition photoresist (A) 0.78 meq/g; (B) 0.96 meq/g.

4. Conclusion

A photosensitive amphiphilic random copolymer UPDES electrodeposition photoresists were prepared. Their chemical, mechanical and thermal properties have been studied. Several conclusions can be drawn from the experimental observations. The UPDHES micelles were mainly a regular sphere-shaped aggregate, the R_h was 51 nm and the hydrodynamic radius distribution was unimodal. A better MEK resistance and Hardness of photoresist film need for additional multi-functional reactive diluent. With the increased of C=C content of photoresist film, the storage modulus and $\tan \delta$ of the films increased owing to higher cross-linking density of the resin system; the thermal stability

decreased because of the thermal dissociation of blocked isocyanates bond. The UPDHES photoresist films had the excellent extensibility especially for the future application in flexible printed circuit board, and had a resolution reach to 15 um that meeting the industrial requirement.

Acknowledgements

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