

Synthesis of Photosensitive Polycarbodiimide

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A negative-working photosensitive polymer based on polycarbodiimide (PCD) and {{{(4,5-dimethoxy-2-nitrobenzyl)oxy}carbonyl)-2-methylpiperidine (1) as a photoamine generator (PAG) has been developed. The end-capped PCDs with number average molecular weights of 1500 and 2500 were prepared by polycondensation of tolylene 2,4-diisocyanate (TDI) in the presence of *m*-tolyl isocyanate and 3-methyl-1-phenyl-2-phospholene-1-oxide as an end-capping agent and a catalyst, respectively. PCDs were amorphous and soluble in common organic solvents, such as toluene, chloroform, and cyclohexanone. Thermo-gravimetry of the polymers showed good thermal stability, indicating that a 10 % weight loss of the polymers was at 480 °C in nitrogen. The PCD films were transparent above 360 nm. The PCD containing 1 showed a sensitivity of 225 mJ/cm² and a contrast of 1.5, when it was post-baked at 90 °C for 90 sec, followed by development with toluene at 25 °C

Keywords: photosensitive polymer, polycarbodiimide, photoamine generator, photosensitivity, contrast, negative type

1. Introduction

Photosensitive polyimides (PSPIs) are widely used as protection and insulation layers in semiconductor manufacturing. They are very attractive since the number of processing steps is reduced by avoiding the use of classical photo resist [1].

We have been interested in developing thermal stable imaging materials which can be used as a substitute of PSPI. In the previous paper [2], we showed a typical thermal stable polymer, poly (ether ether ketone) containing alkyl groups functioned as a negative-type photosensitive polymer.

Polycarbodiimides (PCDs) are easily prepared by self-polycondensation of aromatic diisocyanates in the presence of various phospholene oxides as a catalyst, and converted to cross-linked polymers by thermal treatment. PCDs also react with various nucleophiles such as amine, water and hydrogen sulfide to produce polyguanidines, polyureas and polythioureas, respectively [3].

In the preceding paper [4], we reported the development of new photosensitive polyimide (PI) precursor based on polyisoimide (PII) using an photoamine generator (PAG). PAG liberates a free amine upon irradiation with UV light and the photogenerated amine catalyzes the isomerization of PII to the corresponding PI. This photochemical induced transformation is the basis of generation of negative images. Based on these findings, we expected that the photogenerated amine induces a cross-linking reaction of PCDs by thermal treatment, which gives a dissolution contrast between exposed and unexposed areas. Moreover, this chemistry would be expected to open a new methodology in the design of thermal stable imaging materials.

This paper describes a successful development of negative-working photosensitive polymer consisting of PCD and {{{(4,5-dimethoxy-2-nitrobenzyl)oxy}carbonyl)-2-methylpiperidine (1) as a polymer matrix and a PAG.

2. Experimental

2.1. Materials

N,N-Dimethylacetamide (DMAc) was purified by vacuum distillation and stored over 4-Å molecular sieves. Tetrahydrofuran (THF) and tolylene-2,4-diisocyanate (TDI) were purified by distillation. Tetrafluoroethylene-propylene copolymer (TFP) (AFLAS-170p) was obtained from JSR Co. Ltd.. Other reagents and solvents were obtained commercially and used as received.

2.2. {[(4,5-dimethoxy-nitrobenzyl)oxy]-carbonyl}-2-methylpiperidine (1)

4,5-Dimethoxy-2-nitrobenzyl *p*-nitrophenyl carbonate (DNPP) was prepared according to the previous report in 75 % yield from 4,5-dimethoxy-2-nitrobenzylalcohol and *p*-nitrophenyl chloroformate [4].

A solution of DNPP (3.00 g, 7.94 mmol), 2-methyl piperidine (3.73 mL, 31.8 mmol), and 1-hydroxybenzotriazole (0.322 g, 2.38 mmol) in DMAc (35 mL) was stirred at 90 °C for 24 h. The reaction mixture was then cooled to room temperature and poured into a 1 % aqueous sodium hydrogen carbonate solution (1L). The product was filtered off, washed with water, and dried *in vacuo*. The yield was 2.35 g (87 %). Recrystallization from a mixture of benzene and *n*-hexane (4:7) produced pale yellow needles.

Mp 129-131 °C. IR(KBr): ν 1700 (C=O), 1520 and 1326 cm^{-1} (NO₂). ¹H-NMR (CDCl₃) δ : 1.20 (d, 3H, CH₃), 1.32-1.71 (m, 6H, piperidine), 2.90-3.01 (m, 1H, piperidine), 3.96 (s, 6H, CH₃O), 4.00-4.10 (m, 1H, piperidine), 4.45-4.58 (m, 1H, piperidine), 5.46-5.60 (m, 2H, CH₃O), 7.0 (s, 1H, Ar-H), and 7.70 ppm (s, 1H, Ar-H). ¹³C-NMR (CDCl₃): 154.5 (C=O), 153.2, 147.8, 139.7, 128.6, 109.8, 108.0 (Ar), 63.6 (ArCH₂O), 56.2 (CH₃O), 46.5, 39.0, 30.0, 25.5, 15.8 (methylpiperidino), and 18.4 ppm (CH₃, methyl-piperidino) Anal. Calcd for C₁₆H₂₂N₂O₆: C, 56.80 %; H, 6.55 %; N, 8.28 %. Found: C, 56.99 %; H, 6.69 %; N, 8.26 %.

2.3. Polymer (PCD) synthesis

A solution of TDI (2.43 g, 13.9 mmol) and 3-methy-1-phenyl-2-phospholene-1-oxide (PMO) (0.050 g, 0.26 mmol) in THF (20mL) was heated at 60 °C for 3h. The reaction mixture was then cooled to 30 °C and *m*-tolyl isocyanate (0.40 mL, 2.86 mmol) was added. Subsequently, the reaction mixture was heated at 60 °C for 3 h and poured into *n*-hexane (500mL). The polymer precipitated was collected and dried *in vacuo* at 25

°C. The yield was 2.07 g (85 %). IR(KBr): ν 2120 cm^{-1} (N=C=N). Anal. Calcd for (C₈H₆N₂)_n: C, 73.80 %; H, 4.61%; N, 21.4 %. Found: C, 74.50 %; H, 4.55 %; N, 21.00 %.

2.4. Procedure for photolysis of 1

Photolysis of 1 (5 x 10⁻⁵ mol/L) in solution was carried out using dry, degassed CCl₄. The solution of 1 was charged into quartz cell and was exposed to 365 nm light using a filtered super-high-pressure mercury lamp. The bleaching behavior of exposed solution was then measured by UV analysis. Photolysis in polymer film was performed using TFP as a polymer matrix. The solution of 1, TFP and methyl ethyl ketone (wt%: 5:30:65) was cast on a NaCl plate and dried at 60 °C for 3 min. The films were exposed to 365 nm radiation using a filtered super-high-pressure mercury lamp. The exposed films were then subjected to FT-IR analyses.

2.5. Photosensitivity

The polymer was dissolved in toluene (6 wt%). Two-micron-thick films on a silicone wafer were prebaked at 80 °C for 60 sec, and exposed to 365 nm UV-light using a filtered super-high-pressure-mercury lamp. Exposed films were post exposure baked at 90 °C for 90 sec, developed in toluene at 25 °C, and subsequently rinsed with a mixture of toluene and 2-propanol (1:1). The characteristic sensitivity curve was obtained by plotting a normalized film thickness against the logarithmic exposure energy. Imagewise exposure was carried out in contact mode.

2.6. Measurements

FT-IR spectra were measured on a Horiba FT-210 spectrophotometer. ¹H- and ¹³C-NMR spectra were recorded on a JEOL EX 270 spectrometer. Thermal analyses were performed on a Seiko SSS 5000 TG-DTA 220 thermal analyzer at a heating rate of 10 °C/min for thermogravimetry (TG). Molecular weights were determined by a gel permeation chromatograph (GPC) with polystyrene calibration using JASCO HPLC equipped with Shodex KF-80M column at 40 °C in THF. The film thickness was measured by Dektak 3030 system (Veeco Instrument Inc.).

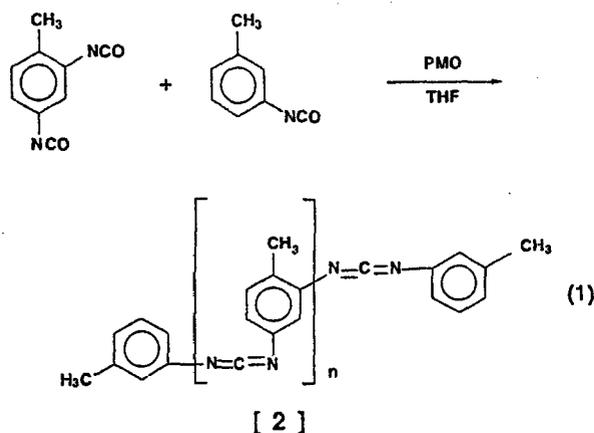
3. Results and Discussion

3.1. Synthesis of End-capped PCDs

As described in the Introduction, PCDs are generally prepared by polycondensation of

aromatic diisocyanates in the presence of phospholene oxides as a catalyst. However, PCDs obtained may contain reactive isocyanate groups at the chain ends, which undergo some side reactions, such as hydrolysis to amine or thermal trimerization to a cross-linking polymer. In order to prevent these side reactions and control the obtained molecular weights of PCDs, the end-capping technique was employed. This leads to polymers having well defined chain ends. TDI was selected as the aromatic diisocyanate due to the high solubility of the resulting PCDs and the availability of monomer. The polycondensation of TDI in the presence of 3-methyl-1-phenyl-2-phospholene-1-oxide was carried out at 60 °C in THF for 3 h and then the end-capping agent *m*-tolyl isocyanate (*m*-TI) was added. The polymer 2 was isolated by pouring the reaction mixture to *n*-hexane. (e.q. 1)

By varying the amount of *m*-TI, PCDs 2a and 2b with number average molecular weights of 2500 and 1500 respectively were prepared.



3.2. Polymer Characterization

The polymers 2 were confirmed as the desired PCDs by IR spectroscopies and elemental analyses. The IR spectra showed a characteristic absorptions at 2120 cm^{-1} due to $\text{N}=\text{C}=\text{N}$ stretching. Elemental analyses also supported the formation of the expected polymer.

Polymers 2 are white solids, soluble in dipolar aprotic solvents, chloroform, cyclohexanone, and THF at room temperature, and are insoluble in methanol, acetone, and *n*-hexane. A transparent film was obtained by casting the polymer solution.

The thermal stability of polymer 2a was examined by thermogravimetry (TG). A typical trace is shown in Figure 1. The polymer is thermally stable and showed a 10% weight loss at 480 °C in nitrogen.

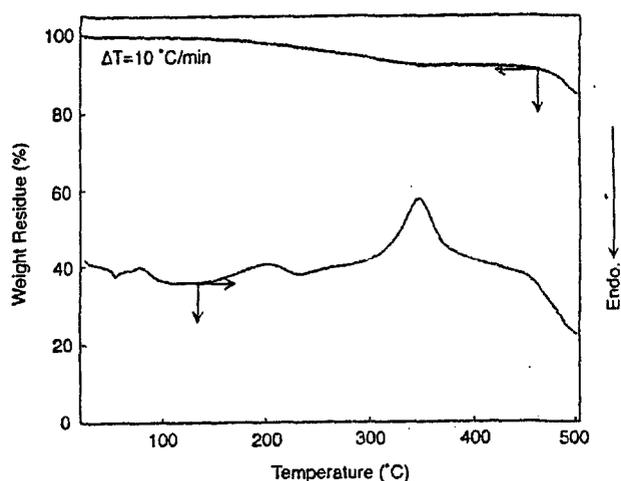


Fig. 1. TG curves of polymer 2 in nitrogen.

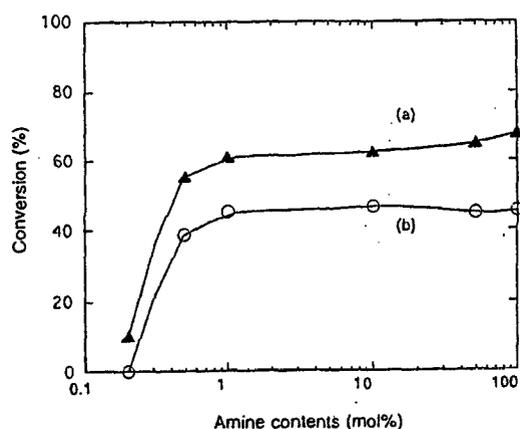


Fig. 2. Relationship between the conversion of polymer 2a and (a) 2-MP, (b) 2,6-DMP.

3.3. Model Reaction

A model reaction was studied to clear the reactivity of secondary amine toward PCDs. The solution of 2a and 2-methyl (2-MP) or 2,6-dimethyl piperidine (2,6-DMP) (15 wt%) in toluene was spin coated on NaCl plate and dried at 80 °C for 3 min. The film was subsequently treated at 100 °C for 3 min on hot-plate. The results are shown in Figure 2. The peak at 2120 cm^{-1} due to the carbodiimide $\text{N}=\text{C}=\text{N}$ stretching band decreased rapidly with increasing the amine content up to 1 mol%, and then remain constant. This quenching of conversion may occur because the T_g of PCD increases with increasing the degree of cross-linking reaction. Furthermore, 2-MP was found to be more effective for the cross-linking reaction than 2,6-DMP because of higher

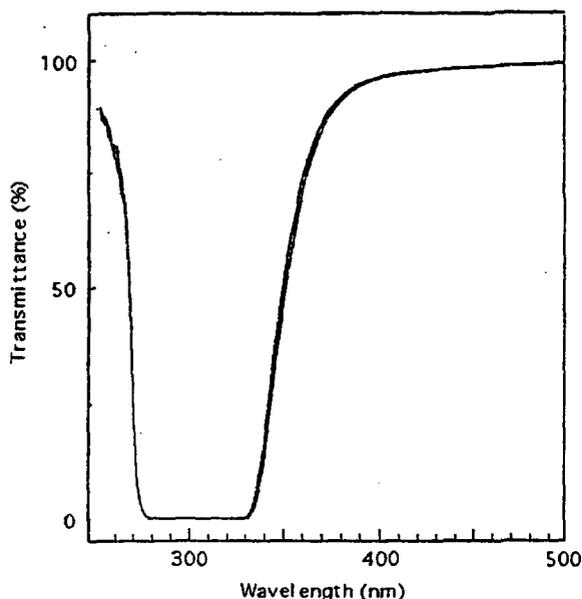


Fig. 3. UV spectrum of polymer 2a film

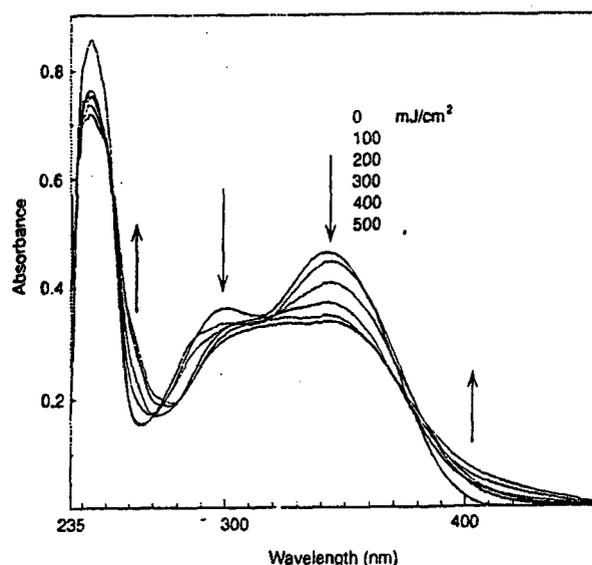
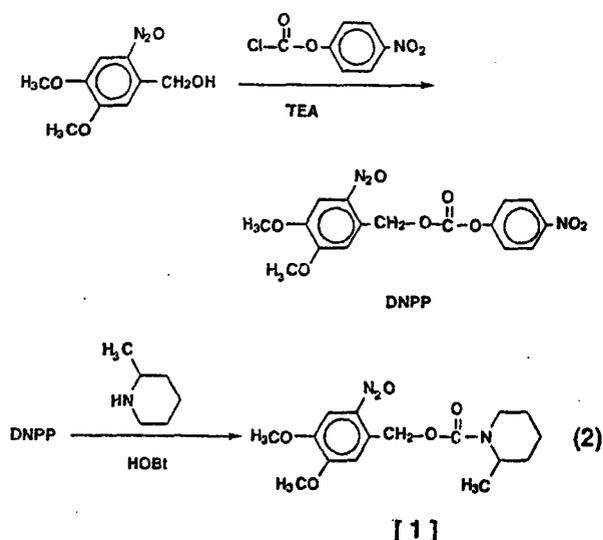


Fig. 4. UV-Visible spectrum of 1.

nucleophilicity. The 2a film without the secondary amine was also heated at 100 °C for 3 min on hot-plate, but no change of the carbodiimide absorption was observed. This indicates that the photogenerated amine will promote the cross-linking reaction.

3.4. Synthesis of [(4,5-dimethoxy-2-nitrobenzyl)oxy]carbonyl 2-methylpiperidine (1)

The photoamine generator 1 was prepared by the reactions shown in the eq. 2.



4,5-Dimethoxy-2-nitrobenzyl alcohol was converted to 4,5-dimethoxy-2-nitrobenzyl *p*-nitrophenylcarbonate (DNPP) by treatment with *p*-nitrophenyl chloroformate. Then, the reaction of DNPP with 2-MP in the presence of 1-hydroxybenzotriazole (HOBt) yielded the new photoamine

generator 1. Recrystallization from a mixture of benzene and *n*-hexane gave pale yellow needles. The structure of 1 was confirmed to be the corresponding carbamate by IR and NMR spectroscopies and elemental analysis. The IR spectrum showed characteristic absorptions at 1700, 1520, and 1326 cm^{-1} due to carbamate carbonyl, nitro asymmetric and symmetric stretching vibrations, respectively. Elemental analysis also supported the formation of the expected structure. In ^{13}C -NMR spectrum of 1, six peaks at 46.5, 39.0, 30.0, 25.5, 18.4, and 15.8 ppm are attributed to the ring and methyl carbons of 2-MP moiety. Moreover, carbamate, *o*-nitrobenzyl, and methoxy carbons appeared at 154.5, 63.6, and 56.2 ppm. Six lower field peaks at 153.2, 147.8, 139.7, 128.6, 109.8, and 108.0 ppm are assigned to the aromatic carbons. Thus, no unaccounted peaks were found, clearly indicating the formation of 1.

3.5. Thermal Stability of photoamine generator 1

Cross-linking reaction is promoted by post-exposure bake (PEB) treatment which requires thermostable PAGs. Then, the thermal stability of 1 was examined by thermogravimetry. Compound 1 was found to be stable up to 250 °C.

3.6. Lithographic Evaluation

Figure 3 shows the UV-visible spectrum of PCD film (1 μm) cast from a 2a/carbon

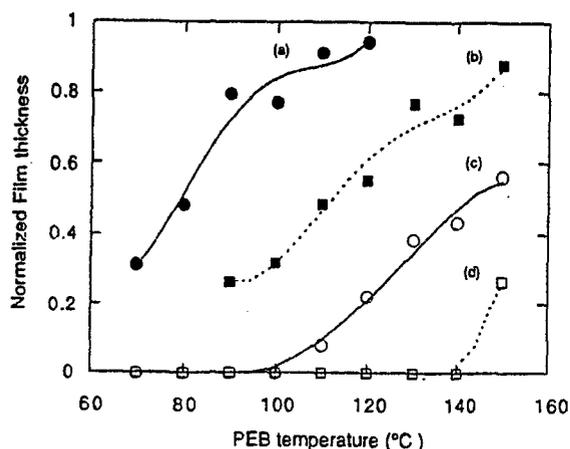


Fig. 5. Relationship between the PEB temperature and the dissolution rate of **2a** ((a); expose, (c); unexpose) and **2b**((b); expose, (d); unexpose) film containing 6wt% of **1**.

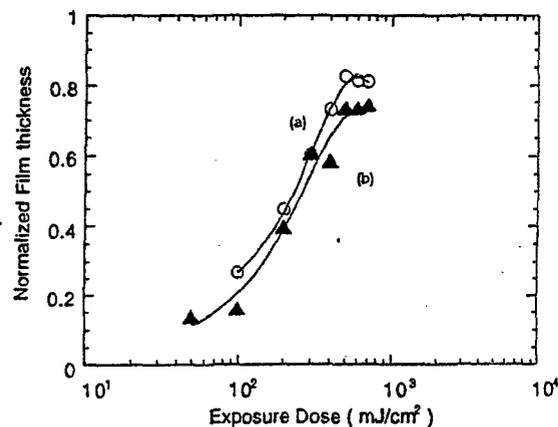


Fig. 6. Sensitivity curve for polymer (a); **2a** and (b); **2b**.

tetrachloride solution (20 wt%). The film is transparent in the region above 360nm. The transmittance of the PCD film is more than 90 %.

The UV-visible spectrum of **1** and its changes upon photoirradiation, are shown in Figure 4. The characteristic absorption bands at 345 nm of **1** decreased upon irradiation with 365 nm light. Furthermore, the conversion of **1** to 2-MP in the polymer film was also followed by FT-IR. We selected tetrafluoroethylene-propylene copolymer (TEF) as a polymer film, because TFP has a high transmittance to UV light, a low moisture sorption and no absorption bands at around 1700 cm^{-1} corresponding a carbamate carbonyl stretching band. The TFP solution containing 5 wt% of **1** was spin-coated on NaCl plate and dried 60°C for 3 min and then, 365 nm light was exposed. The rapid decrease of characteristic absorption bands at 1700 and 1530 cm^{-1} due to carbamate carbonyl and nitro asymmetric stretching vibrations, respectively, were clearly observed. These results indicate compound **1** releases 2-MP upon irradiation and this photopolymer system would be expected to be lithographically sensitive to the 365 nm UV radiation.

In chemically amplified photopolymer systems, chemical transformations are accomplished by heating the exposed film, that is, a post-exposure baking (PEB) is one of the key steps to obtain the desired photochemical process. Figure 5 shows the relationship between the PEB temperature and the dissolution behavior of the **2a** film containing 6 wt% of **1** after exposure (500 mJ/cm^2).

Dissolution rate of the exposed area decreased drastically due to the cross-linking reaction induced by the photogenerated 2-MP. The dissolution rate difference between the exposed and unexposed areas reached the maximum in polymer **2a** and **2b** at 90 °C and 130 °C, respectively. At higher temperatures thermal cross-linking reactions were observed in unexposed areas of polymers, **2a** and **2b**.

After a preliminary optimization study involving developing solvent, prebake temperature, the photosensitivity of polymer was evaluated under the following process conditions. Polymer **2** (14 wt%) and compound **1** (6 wt%) were dissolved in toluene (80 wt%). The solution was spin-coated onto a silicon wafer, followed by heating at 80 °C for 1 min, irradiated to 365 nm light, post exposure baked at 90 °C for 90 sec and then developed with toluene at room temperature. The sensitivity curve for a 2 μm thick film shown in Figure 6 indicates that the sensitivity ($D_{1/2}$) and the contrast ($\gamma_{1/2}$) of **2a** and **2b** were 225 mJ/cm^2 and 1.53, respectively. In Figure 7 is presented a scanning electron micrograph of the contact-printed image that was obtained the polymer **2a** film after exposure to 500 mJ/cm^2 . This polymer is capable of resolving 6 μm feature without thinning and swelling of patterns when a 3 μm thick film was used. On the other hand, polymer **2b** gave the swollen images, probably due to its low molecular weight. To investigate the thermal stability of polymer film, this negative image in the polymer **2a** film was thermally treated in the

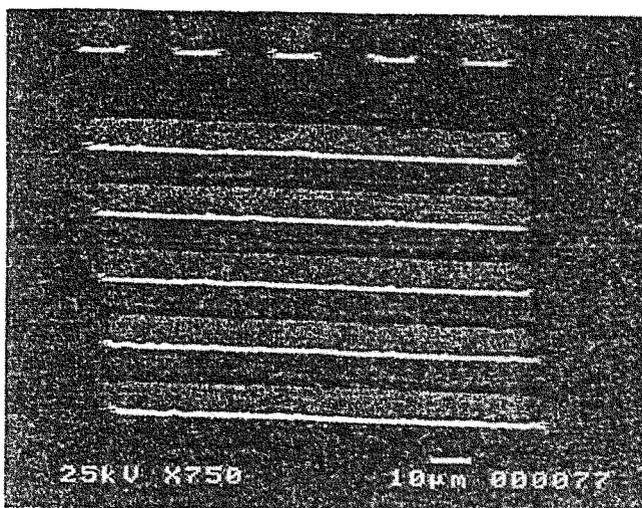


Fig. 7. Scanning electron micrograph of patterns printed from polymer 2a.

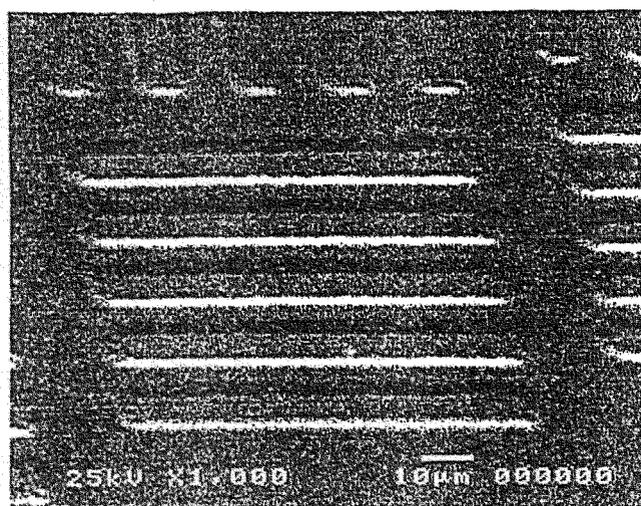
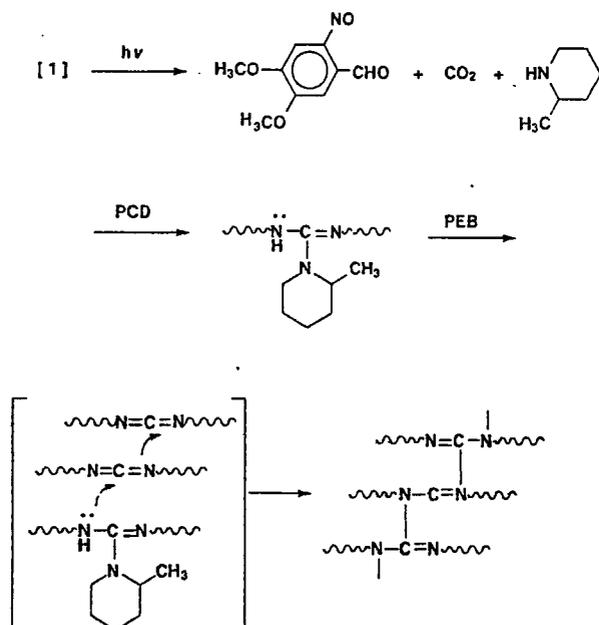


Fig. 8. Scanning electron micrograph of thermally treated patterns.

following steps: 200°C for 2 h, 300 °C for 2 h, and 400 °C for 2 h. As shown in Figure 8, the resulting negative image in the 2a film was very stable and hadn't any deformation.



Scheme 1. The mechanism of negative pattern formation.

The mechanism of a negative pattern formation is outlined in Scheme 1.

A photogenerated amine reacts with carbodiimide linkages to give guanidine units, which undergo further addition reactions to polymers 2 by PEB. This reaction converts soluble polymers

2 to insoluble cross-linked polymers.

4. Conclusion

The end-capped and molecular weight controlled polymers 2 were prepared by polycondensation of TDI in the presence of *m*-tolyl isocyanate and 3-methyl-1-phenyl-2-phospholene-1-oxide as an end-capping agent and a catalyst, respectively. Polymers 2 were soluble in common organic solvents, such as toluene, chloroform, and cyclohexanone, and thermally stable up to 450 °C. Polymer 2a containing 6 wt% of 1 functioned as a negative type photopolymer, its sensitivity and contrast were 225 mJ/cm² and 1.5 at 365 nm light, respectively.

Acknowledgement

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References

1. T. Omote, "polyimides" M. Ghosh and K. L. Mittal, Eds., Dekker, New York, 1996, p. 121
2. M. Ueda, T. Nakayama, and T. Mitsuhashi, *J. Polym. Sci. Part-A, Polym.*, **35**, 371, (1997)
3. C. D. Eisenbach and H. Netzger, "Handbook of Polymer Synthesis" H.R. Kricheldorf, Eds., Marcel Dekker, Inc., New York, 1992, Part A, p.730.
4. A. Mochizuki, T. Teranishi, and M. Ueda, *Macromolecules*, **28**, 365 (1995).