Polymer Bulletin 47, 175–181 (2001)

Polymer Bulletin

Photosensitive polycarbonates based on reaction development patterning (RDP)

Toshiyuki Oyama (✉), Yukiko Kawakami, Takafumi Fukushima, Takao Iijima, Masao Tomoi (✉)

Department of Advanced Materials Chemistry, Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
e-mail: oyama@ynu.ac.jp, Tel.:/Fax: +81-45-339-3962

Received: 11 July 2001/Accepted: 1 August 2001

Summary

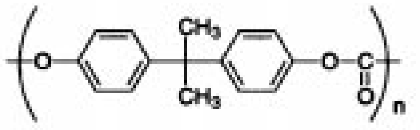
Films of commercially available poly(bisphenol A carbonate) (BPA-PC) and poly[bisphenol A carbonate-*co*-4,4'-(3,3,5-trimethylcyclohexylidene)diphenol carbonate] (BPA-TMC-PC) containing photosensitive agent (diazonaphthoquinone (DNQ) compound) were prepared by spin-coating onto copper foil. The obtained films showed positive-tone behavior by UV irradiation and following development with ethanolamine/*N*-methylpyrrolidone (NMP)/H_2O mixture (1/1/1 by weight). The scanning electron microscope (SEM) photographs of the resulting images exhibited fine patterns (~10 µm line/space resolution) with 15-16 µm film thickness. The pattern forming mechanism is based on the Reaction Development Patterning (RDP), in which the carboxylic acid resulting from photo-rearrangement of DNQ in the film attracts ethanolamine in the developer and the amine reacts with carbonate in the main chain to induce degradation of the polymer. RDP, where the main pattern forming reaction occurs during the development, is proved to be efficient for polycarbonates as well as polyimide.

Introduction

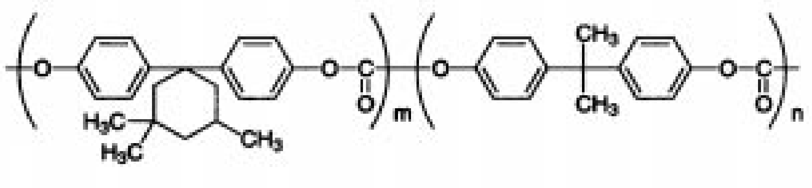
Photosensitive polymeric materials have been used as photoresists for production of semiconductor chips [1-2]. Especially, combination of novolac resins as binder polymers and diazonaphthoquinone (DNQ) compounds, which are sensitive to 360-450 nm light, as dissolution inhibitors has widely been utilized as positive photoresists for microlithography [1]. The pattern formation in this system is based on photo-rearrangement of DNQ to indenecarboxylic acid which behaves as dissolution accelerator. Photosensitive polymers with photo-radical or -acid generators, where species generated by photo-irradiation initiate polymerization or react with functional groups in the polymers, have also been investigated [2-4]. However, in the systems mentioned above, essential chemical reactions for photoresist property occurs *before* development process: In development, only dissolution of polymers and/or simple reaction such as acid-base reaction occur.

On the other hand, in the course of the study of photosensitive polyimides (PSPIs) used for photo-patternable insulating materials [5], we prepared novel type of PSPIs with principally different pattern-forming process from classical photoresists, i.e. Reaction Development Patterning (RDP) [6]. In RDP process, main chemical reaction for pattern formation is the reaction of the polymer main chain with developer *in* development process. Photosensitive materials in this photoresist system have a role to differentiate permeability of developer into exposed area from that into unexposed area. The reaction during development induces main-chain scission and resulting depolymerization to give high solubility of depolymerized region into the developer. This RDP process has advantage that no special functional group or photosensitive group is needed for emergence of photoresist properties, except the groups in the main chain that can react with the developer. In the case of PSPIs, combination between multi-block copolyimides without any pendant alkaline-reactive groups as matrix resins and DNQ compounds as photosensitive materials was used. The obtained PSPIs actually showed good positive-tone behavior by UV irradiation and the following reaction of imide ring with ethanolamine in the developer, and GPC profiles of PSPI after irradiation and development proved main-chain scission by the amine [6].

RDP process based on DNQ compound as photosensitive agent and amine as developer can be applied to other polymers having carbonyl linkages in the main chain. This paper depicts the application of commercially available polycarbonates, which contain carbonate linkages in the main chain, for novel photo-patternable materials by the use of RDP. Polycarbonates are versatile engineering plastics with good dimensional stability, high transparency and impact strength [7]. Though they are known to receive nucleophilic attack at the carbonyl linkage, to our knowledge, there has been no example of utilization of commercial polycarbonates as photoresist [8]. Thus, giving photoresist properties to commercial polycarbonates will offer a promising prospect of preparation of novel photoresists. Here, utilization of commercially available poly(bisphenol A carbonate) (BPA-PC, Scheme 1) and poly[bisphenol A carbonate-*co*-4,4'-(3,3,5-trimethylcyclohexylidene)diphenol carbonate] (BPA-TMC-PC, Scheme 1) as photosensitive PCs based on RDP by combining with a DNQ compound, 1,2-naphthoquinonediazide-5-sulfonic acid *p*-cresol ester (PC-5®) (Scheme 2) is described.

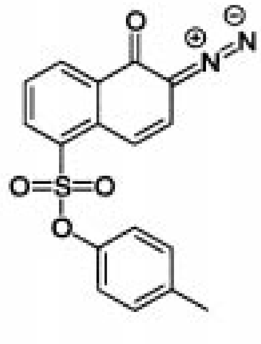


Poly(bisphenol A carbonate) (BPA-PC)



Poly[bisphenol A carbonate-*co*-4,4'-(3,3,5-trimethylcyclohexylidene)diphenol carbonate] (BPA-TMC-PC, m : n = 30 : 70 (^{1}H-NMR))

Scheme 1. Structure of polycarbonates



Scheme 2. 1,2-Naphthoquinonediazide-5-sulfonic acid *p*-cresol ester (PC-5®)

Experimental

Materials

Poly(bisphenol A carbonate) (BPA-PC) and poly[bisphenol A carbonate-*co*-4,4'-(3,3,5-trimethylcyclohexylidene)diphenol carbonate] (BPA-TMC-PC, the ratio between BPA and TMC units was found to be *ca*. 70:30 in ^{1}H-NMR spectrum) were purchased from Aldrich. 1,2-Naphthoquinonediazide-5-sulfonic acid *p*-cresol ester (PC-5$^{®}$) was obtained from Toyo Gosei Kogyo Co., Lid. Other reagents and solvents were purchased from commercial sources and were used as received.

Instrument

^{1}H-NMR spectra were obtained with a JEOL JNM-EX270 spectrometer (270 MHz) in chloroform-*d* at 60 °C. Gel permeation chromatographic analyses (GPC) by using *N,N*-dimethylformamide (DMF) containing LiBr (30 mmol/L) and phosphoric acid (60 mmol/L) as an eluent were carried out on a Tosoh DP-8020 and UV-8020 (TOSOH TSK$_{gel}$ GMH$_{HR}$-M column, eluting rate 1000 μL/min) after calibration with standard polystyrene. UV-Vis absorption spectra were measured with a Shimadzu UV-2000 spectrophotometer. Thickness of PC films was measured with a Nanometrics Nanospec/AFT Model 3000 non-contact type optical film thickness analyzer. Irradiation was carried out by a UV exposure apparatus (ORC JP-2000-EXC) and exposure dose was measured at 320-390 nm (ORC UV-331AP2). The microstructure of the developed films was observed with a JEOL JSM-5500LV scanning electron microscope (accelerating power: 10 kV) after the pattern surface was coated with a thin layer of Au by using ion sputtering apparatus.

Preparation of PC films with photosensitive agent

Polycarbonate (BPA-PC or BPA-TMC-PC, 20 g) was dissolved in *N*-methylpyrrolidone (NMP, 60g) at 180 °C. Into the obtained varnish (16 g) were added the diazonaphthoquinone (DNQ) compound PC-5$^{®}$ (Scheme 2) as photosensitive agent (1.2 g, 30 wt% of the polymer) and NMP as diluent (4 g). The resultant photosensitive PC was degassed and spin-coated onto a mat side of copper foil. The succeeding prebaking in a far-infrared oven (90 °C, 10 minutes) afforded the films with 15-16 μm thickness.

Irradiation and Development

The films on copper foil were irradiated with ultra high-pressure mercury lamp without filter at both i- and g-lines (2000 mJ/cm^2) through a positive photomask by contact technique. The exposed films were developed by dipping in ehtanolamine/NMP/H_2O mixture (1/1/1 by weight) at 40 °C for 7-10 minutes, and rinsed with pure water.

Results and discussion

Sensitivity and contrast of photosensitive polycarbonates

Photosensitive polycarbonates (PSPCs) were easily formulated by dissolution of commercially available poly(bisphenol A carbonate) (BPA-PC) and poly[bisphenol A carbonate-*co*-4,4'-(3,3,5-trimethylcyclohexylidene)diphenol carbonate] (BPA-TMC-PC) in NMP and following addition of photosensitive DNQ compound PC-5® (Scheme 2, 30 wt% of polycarbonate). The sensitivity of the resulting PSPCs was investigated by irradiation of the UV light (> *ca*. 360 nm) onto PSPC films with various exposure doses. The irradiated films were developed by dipping with ethanolamine/NMP/H_2O mixture (1/1/1 by weight) at 40 °C. The relationship between exposure dose and normalized film thickness (sensitivity curve) of PSPC from BPA-PC was shown in Figure 1, and the curve showed positive-tone behavior. Sensitivity (E_0), which was estimated from the exposure dose where exposed film was completely dissolved into the developer and the copper-foil surface appeared, was found to be about 1000 mJ/cm^2. Contrast (γ value) obtained from slope of the curve was 0.93. E_0 and γ of PSPC from BPA-TMC-PC were 1000 mJ/cm^2 and 0.74, respectively. These results show that PSPCs simply prepared by mixing commercially available PCs with DNQ compound can actually be used as photoresist films.

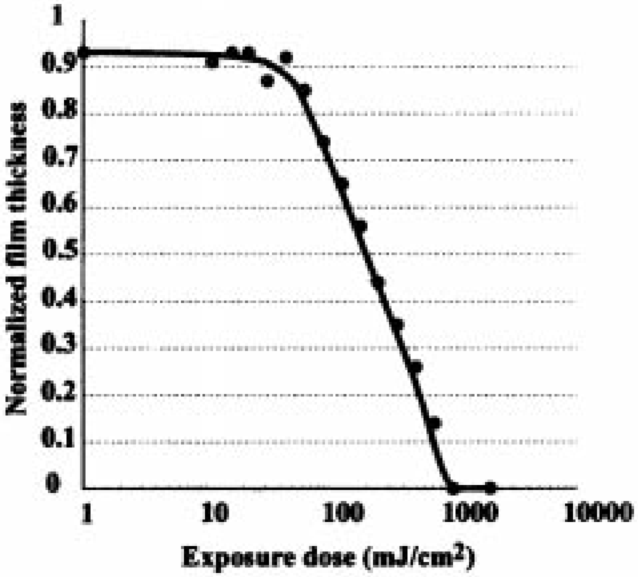


Figure 1. Sensitivity curve for positive PSPC from BPA-PC and 30 wt% PC-5®

Lithographic evaluation

To evaluate lithographic potential of PSPCs, the films prepared by spin-coating of PSPC varnishes onto copper foil were irradiated by UV light containing both i- and g-lines through a photomask, and developed by dipping with ethanolamine-containing developer at 40 °C. Figure 2 indicates the representative line/space (L/S) patterns of PSPCs obtained from SEM analysis.

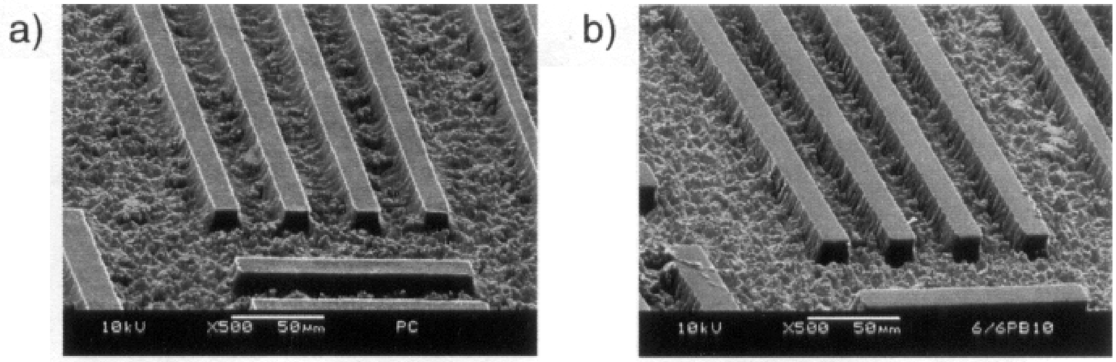


Figure 2. SEMs of L/S patterns for positive PSPCs with 30 wt% PC-5®: a) PSPC from BPA-PC; b) PSPC from BPA-TMC-PC

Clear and sharp L/S patterns at ~10 μm dimension were obtained without any peeling-off, swelling and deformation in both homo- and copolymer films with 15-16 μm thickness. Some tapering form was observed in the obtained patterns, and side walls of the resulting images seemed to be affected by the fine structure of copper-foil surface. Hard thin layer was also observed at the top of the line patterns. This layer is considered to be formed in prebaking step, where the evaporation of the solvent (NMP) from the films would be most efficient at the surface, and as a result, the hard skin was obtained. It must be this hard layer that maintains initial thickness of the unexposed area of the films after development and leads to high aspect ratio in this system. From these results, the ability of PSPCs as novel kind of photoresist is evidenced. Optimization of irradiation and development conditions will enable the formation of patterns with higher resolution.

Pattern forming mechanism based on RDP

Figure 3 shows GPC profiles of the original BPA-PC and exposed area of photo-irradiated PSBPA-PC after development. GPC profile of the exposed region exhibited only low molecular-weight peak, though the original polycarbonate had M_n = 20,000. This result indicates that PSPC is dissolved in the developer as depolymerized products and implies that PSPC is decomposed during development [6].

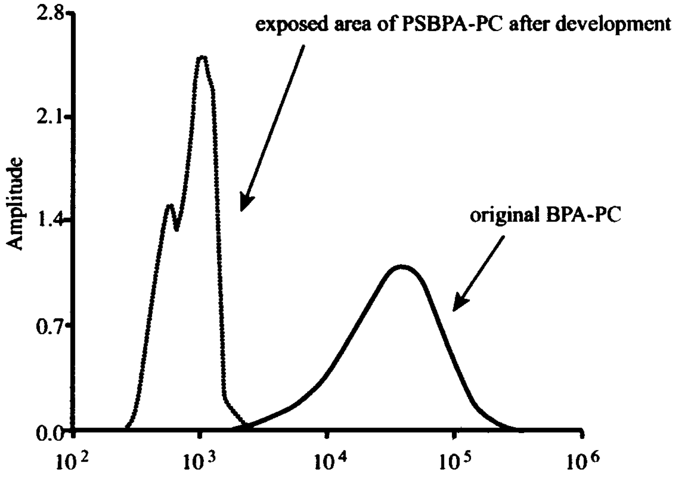
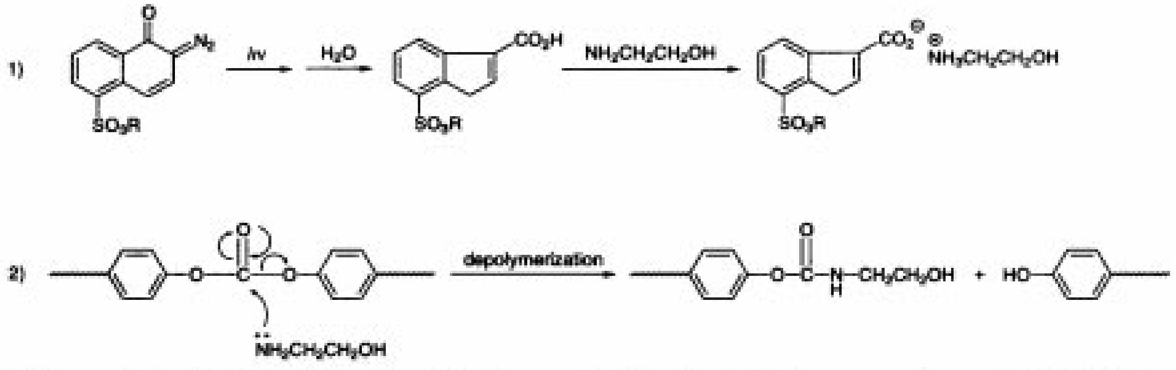


Figure 3. GPC profiles of the original BPA-PC (solid line) and of exposed area of PSBPA-PC after development (dashed line)

Therefore, the patterns of PSPC films are thought to be obtained by Reaction Development Patterning (RDP), proposed by us for photosensitive polyimides without any specific functional groups [6]. This new patterning differs from chemical amplification patterning in that the former involves pattern-forming reaction *during* development, while main chemical reaction in the latter occurs *before* development.

RDP is based on difference in affinity for the developer between exposed and unexposed areas, and is considered to proceed as shown in Scheme 3; Photosensitive DNQ compound in exposed region rearranges to alkaline-soluble indenecarboxylic acid derivative *via* formation of indeneketene and the succeeding reaction with H_2O. The carboxylic acid then reacts with ethanolamine in the developer at the interface between the surface of the exposed area and the developer to afford ammonium salt, which is believed to promote permeation of the hydrophilic developer into the exposed polycarbonate matrix. The permeated ethanolamine induces depolymerization of polycarbonates by nucleophilic attack of the amine to carbonate linkage to give low molecular-weight products as shown in the GPC profile (Figure 3).



Scheme 3. Mechanism of Reaction Development Patterning (RDP) process for positive PSPC with DNQ compound at exposed area in developer containing ethanolamine

On the other hand, the unreacted, hydrophobic DNQ compound in the unexposed area suppresses diffusion of the amine into PC matrix to give polycarbonates the increased insolubility into the developer. Thus, the presence of photosensitive material in PSPCs is definitely important due to its dual role both as accelerator in the exposed area and as inhibitor in the unexposed area.

Conclusions

Photosensitive polycarbonates prepared by mixing commercially available polycarbonates with photosensitive DNQ compound showed good positive photosensitivity by UV irradiation and the following development with solution containing ethanolamine. The resulting pattern had ~10 µm L/S resolution with 15-16 µm film thickness, and molecular weight of polycarbonates at exposed area was decreased by development using amine-containing developer. From these results, polycarbonates are considered to show positive-tone behavior by Reaction Development Patterning (RDP) mechanism, where the carboxylic acid formed by photo-rearrangement of DNQ increases the affinity of exposed area for ethanolamine and the amine diffused in polycarbonate matrix reacts with carbonate linkage to degrade the polymer. RDP process, which has been proposed for photosensitive polyimides, is found to be extended to pattern formation of polycarbonates. Further utilization of RDP will expand the scope of design for photoresist, and application of RDP for other polymers containing various linkages such as ester and amide is in progress.

References

1. Reichmanis E, MacDonald SA, Iwayanagi T, Eds (1989) Polymers in Microlithography, Materials and Processes. ACS Symposium Series 412. American Chemical Society, Washington DC
2. Roffey C (1997) Photogeneration of Reactive Species for UV Curing. Wiley, Chichester
3. Decker C (1996) Prog Polym Sci 21:593
4. Lohse F, Zweifel H (1986) Adv Polm Sci 78:61
5. Horie K, Yamashita T, Eds (1995) Photosensitive Polyimides. Technomic, Lancaster
6. Fukushima T, Oyama T, Iijima T, Tomoi M, Itatani H (2001) J Polym Sci Part A Polym Chem in press
7. Freitag D, Fengler G, Morbitzer L (1991) Angew Chem Int Ed Engl 30:1598
8. An example of utilization of aliphatic polycarbonates containing base-releasing cobalt (III) photoinitiator as positive-tone photosensitive materials: Davies JD, Daly WH, Wang Z, Kutal C (1996) Chem Mater 8:850