

Developments of Photosensitive Polyimides and Photosensitive Polybenzoxazoles

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Introduction

Polyimides (PIs) and Polybenzoxazoles (PBOs) are used as insulation materials in microelectronics, because they possess excellent thermal stability and mechanical properties, solution processability, and reasonably low dielectric constants. The fabrication of electronic devices containing metal wiring embedded in PIs is simplified using photosensitive polyimides (PSPIs) and polybenzoxazoles (PSPBOs). Otherwise, an additional photoresist is required for patterning of PI or PBO film, involving additional complicated process steps. Creation of PSPIs and PSPBOs capable of being developed in alkaline is also a benefit in terms of the environment. In this presentation, our recent studies on development of PSPIs and PSPBOs are introduced.

i. Direct patterning of poly(amic acid) (PAA) and low-temperature imidization using a photo-base generator.¹

Direct use of the PAA polymerization solution prepared from tetracarboxylic dianhydride with a diamine in aprotic amidic solution (*e.g.*, DMAc, *N*-methyl-2-pyrrolidone) simplifies the photolithography process. Furthermore, low-temperature thermal imidization of the negative image in this PSPI system also is described.

Base-catalyzed imidization of PAA with dimethyl piperidine (DMP)

The Upirex[®]-type PAA derived from oxydianiline (ODA) and 4,4'-bipthalic dianhydride (BPDA) was used as a matrix. To investigate the thermal imidization of PAA with DMP up to 200°C, the reaction was monitored with FTIR spectroscopy.

First, the effect of DMP loading in the PAA film and the influence of temperature on the degree of imidization was investigated (Figure 1a). The degree of imidization was 86% for base-free PAA at 200°C. In contrast, even in the presence of 2 wt% DMP, imidization was accelerated, producing PI at 200°C. Addition of 5 or 10 wt% DMP further accelerated imidization, which reached 100% at 180 and 190°C, respectively.

Second, the time dependence of imidization in the presence of 10 wt% DMP was studied at 140 and 160°C, and compared with the additive-free PAA film. Figure 1b

shows significant imidization of 10 wt% DMP-containing PAA at 160°C within 10 min. The other conditions were not effective for imidization, and even extending the heating time up to 1 h. Secondary amines, such as DMP, also worked well for solid-phase low-temperature imidization of PAAs and can be used as PBG for negative-type PSPI.

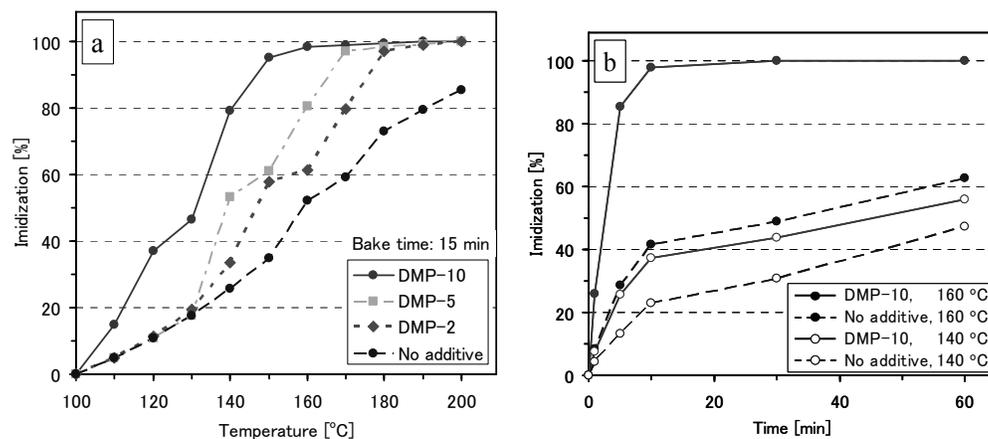


Figure 1. (a) Effect of DMP loading in the PAA film and temperature for thermal treatment on the degree of imidization. Thermal treatment time is fixed for 15 min at each temperature. (b) Effect of thermal treatment time on the degree of imidization.

Lithographic evaluations

To obtain contrasting pattern profiles from exposed and unexposed areas, the effects of PBG loading, PEB temperature, composition of developer, and exposure dose were investigated. Films were obtained by spin-casting the diluted polymerization solution of PAA (10 wt%) containing $\{[(4,5\text{-dimethoxy-2-nitrobenzyl})\text{oxy}]\text{carbonyl}\}$ -2,6-dimethyl piperidine (DNCDP) (0-20 wt%) as a photobase generator on a silicon wafer, and then pre-baking at 100°C for 2 min in air. This photosensitive polymer film was irradiated with UV light at 365 nm (i-line) using a filtered super-high-pressure mercury lamp, baked after exposure (post-exposure baked, PEB) at a set temperature, and developed with TMAHaq/10 wt% iPrOH at 25°C.

The effect of DNCDP level on dissolution rate of the polymer film was studied. Dissolution rate was estimated by the change in film thickness before and after development. As shown in Figure 2, dissolution rate in the exposed area decreased with increasing DNCDP content when exposure dose and PEB were fixed at 1000 mJ/cm² and 160°C, respectively, for 5 min. Dissolution rate in the exposed area decreased 370-fold in the presence of 15 wt% DNCDP.

Next, the effect of PEB temperature was studied; results are shown in Figure 3. A PEB temperature of 160°C for 5 min was required to achieve suitable contrast in

dissolution rate; temperatures below 150°C were not sufficient to inhibit dissolution. Thus, the PEB temperature is critical to lithographic evaluation of PAA imidization.

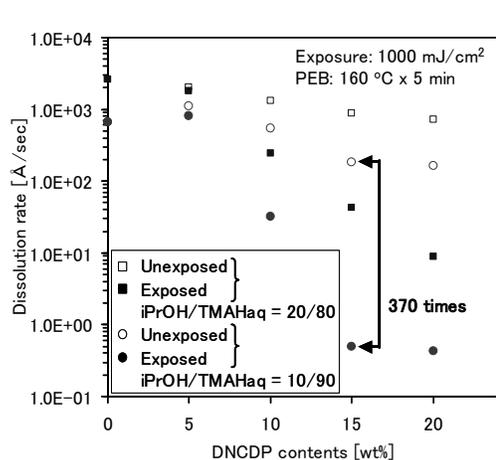


Figure 2. Effect of DNCDP content on the dissolution rate of PAA-2 film. The films irradiated 1000 mJ/cm² of i-line were developed with TMAHaq/20 wt% iPrOH (■: exposed, □: unexposed) or 10 wt % iPrOH (●: exposed, ○: unexposed).

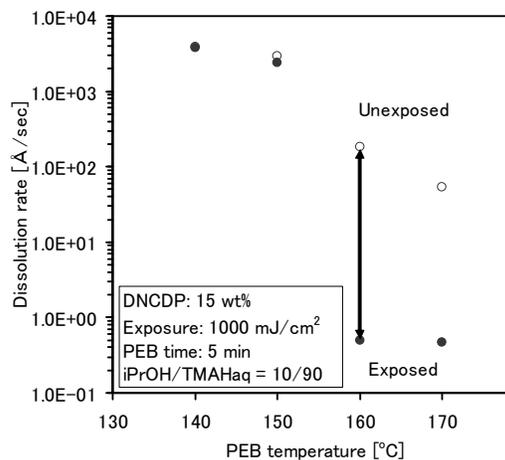


Figure 3. Effect of PEB temperature on the dissolution rate of 15 wt % DNCDP-containing PAA-2 film for 5 min. The films irradiated 1000 mJ/cm² of i-line were developed with TMAHaq/10 wt % iPrOH (●: exposed, ○: unexposed).

Based on these preliminary optimization studies, a photosensitive polymer consisting of PAA-2 (85 wt%) and DNCDP (15 wt%) was formulated. The photosensitivity curve of a resist film 1.0 μm thick is shown in Figure 4 (PEB treatment was conducted at 160°C for 5 min and developed with TMAHaq/10 wt% iPrOH). This resist system had the sensitivity ($D_{0.5}$) of 220 mJ/cm² and contrast ($\gamma_{0.5}$) of 11.7 with i-line.

Image formation of PAA-2 with DNCDP system

Figure 5 depicts an SEM image of a contact-printed pattern obtained with 2.4-μm resist film exposed with i-line of 1000 mJ/cm², PEB at 160°C for 5 min, developed with TMAHaq/10 wt% iPrOH in an ultrasonic bath for 8 min at 40°C, and cured at 200°C for 10 min. A clear negative-tone image with an 8-μm line-and-space resolution was obtained.

Thermal imidization

To study imidization using IR spectroscopy, the PAA films containing DNCDP were baked on a hotplate at designated temperatures, such as a pre-bake at 100°C for 3 min,

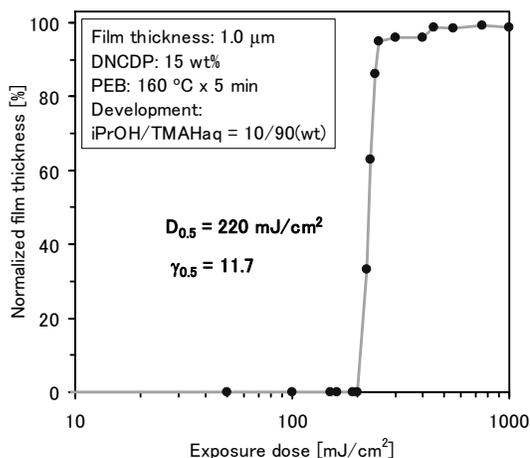


Figure 4. Photosensitivity curve of PSPI consisting of PAA-2 (85 wt %) and DNCDP (15 wt %) in 1.0- μm thickness.

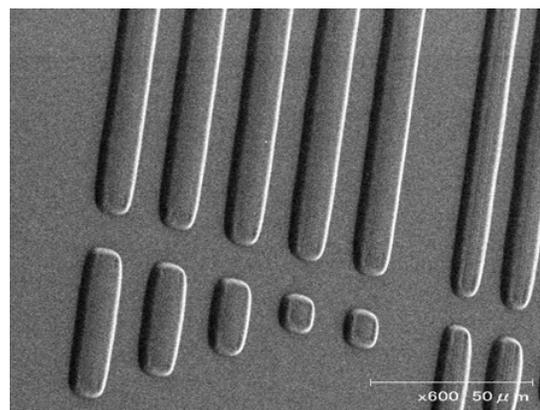


Figure 5. SEM image of PSPI patterns based on PAA-2 (75 wt %) and DNCDP (25 wt %).

PEB at 160°C for 5 min after exposure (1000 mJ/cm² of i-line), and a cure temperature of 200°C for 10 min. A reference PI-2 film was prepared by the following thermal treatment, such as at 200 and 250°C, respectively, for 0.5 h, and finally at 350°C for 1 h in air. Figure 6 shows IR spectra of PAA-2 films containing 15 wt% DNCDP upon exposure with i-line, followed by heat treatment at each temperature level (100, 160, and 200°C). Although the IR spectrum after PEB treatment indicates incomplete imidization (Figure 6b), the IR spectrum after curing at 200°C was identical to that of the fully cured PI film (Figure 6c, d). These results indicate that photochemically generated DMP and DMP produced by thermal decomposition of DNCDP are good catalysts for imidization of PAA.

Summary

A negative-type photosensitive polyimide (PSPI) was formulated from a PAA polymerization solution with a photo-base generator (PBG). The photosensitivity and contrast of 1.0- μm thick resist film consisting of PAA-2 (85 wt%) and DNCDP (15 wt%) were 220 mJ/cm² and 11.7, respectively. PAA-2 containing 25 wt% DNCDP produced a clear negative-tone image with 8- μm features. This pattern can be converted subsequently into the corresponding PI-2 upon heating at 200°C. This new patterning process and low-temperature imidization for PSPIs potentially provide a more efficient and versatile patterning process for PSPIs compared to the standard route that requires the modification of PAAs and high imidization temperatures.

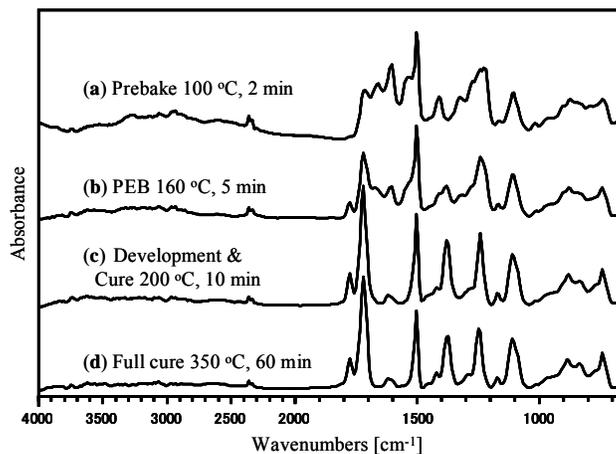
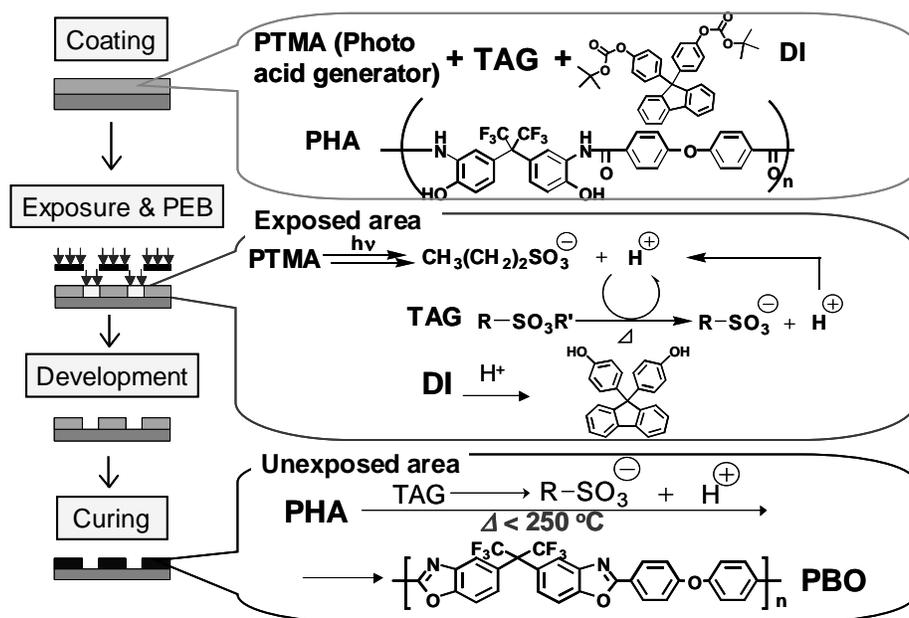


Figure 6. IR spectra of PAA-2 film containing DNCDP at each step: (a) spin-cast on a silicon wafer and pre-baked at 100 °C for 2 min; (b) after exposure to i-line and PEB at 160 °C for 5 min; (c) after development with TMAHaq/10 wt% iPrOH and subsequent cure at 200 °C for 10 min; (d) final full-cured film at the elevated temperature up to 350 °C for 1 h in air.

ii. Photosensitive polybenzoxazole based on poly(*o*-hydroxy amide), dissolution inhibitor, thermoacid generator, and photoacid generator ²

The sensitivity of photopolymers is important in the design of photoresist materials. The conventional PSPBO based on DNQ, however, possesses low sensitivity (>100 mJ/cm²) and a strong absorbance at 365 nm, and is difficult to use for thick patterns. Furthermore, high thermal treatment is required for conversion poly(*o*-hydroxy amide) (PHA) to a PBO. To overcome these problems, this section shows the successful development of an alkaline-developable, chemically amplified positive-type PSPBO based on a PHA, a dissolution inhibitor (DI), 9,9-bis(4-*tert*-butoxycarbonyloxyphenyl)fluorene (*t*-BocBHF), a thermoacid generator (TAG), isopropyl *p*-toluenesulfonate (ITS), and a photoacid generator (PAG), (5-propylsulfonyloxyimino-5*H*-thiophene-2-ylidene)-(2-methylphenyl)acetonitrile (PTMA). A patterning process and subsequent low-temperature cyclization using PSPBO is shown in Scheme 1.



Scheme 1. Patterning process and subsequent low-temperature cyclization using positive-type PSPBO.

Lithographic Evaluation of the PHA/DI/TAG/PAG system.

Preliminary optimization studies of processing conditions and composition ratios of DI, TAG, and PAG to PHA for formulation of new PSPBOs were conducted using *t*-BocBHF and PTMA as the DI and a PAG, respectively. Films were obtained by spin-casting a diluted solution of PHA, DI, TAG, and PTMA in cyclohexanone on a silicon wafer, and then pre-baked at 100°C for 5 min in air. This photosensitive polymer film was irradiated with UV light (100 mJ/cm²) at 365 nm (*i*-line) using a filtered super-high-pressure mercury lamp, baked after exposure at a set temperature for 3 min, and developed with TMAHaq/2.5wt% *i*PrOH at 25°C.

Post-exposure baking (PEB) temperature is crucial for chemically amplified resist systems because diffusion of the generated acids in the films is a key process. To clarify the dissolution behaviors of PSPBO films containing *t*-Boc BHF, ITS, and PTMA in both exposed and unexposed areas, the dissolution rate was estimated by the change in film thickness before and after development. As shown in Figure 7, a large difference in dissolution (dissolution contrast, DC) of approximately 800 times between the exposed and unexposed areas in 2.38 wt% TMAHaq/2.5wt% *i*-PrOH was obtained for PEB at a temperature range of 120°C, indicating that the photo-generated acid decomposes *t*-Boc BHF effectively to give BHF by PEB treatment. PEB temperatures greater than 130°C may induce thermal decomposition of *t*-Boc BHF, resulting in greater solubility in 2.38

wt% TMAHaq/2.5wt% *i*PrOH.

The effect of PEB time on dissolution rate of the film was investigated as shown in Figure 8. PEB times of 3-4 min were adequate to produce a large DC between exposed and unexposed areas. Further PEB treatment may induce decomposition of TAG, resulting in no DC between the exposed and unexposed areas.

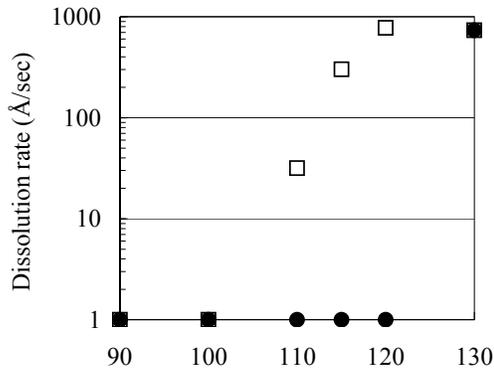


Figure 7. Effect of PEB temperature on dissolution rate for PHA/*t*-Boc BHF/ITS/dissolution rate for PHA/*t*-Boc BHF/ITS/PTMA (73/18/7.5/1.5 wt/wt/wt/wt) resist system in exposed (□) and unexposed (●) areas. The *i*-line exposure and PEB time were fixed at 100 mJ/cm² and 3 min, respectively.

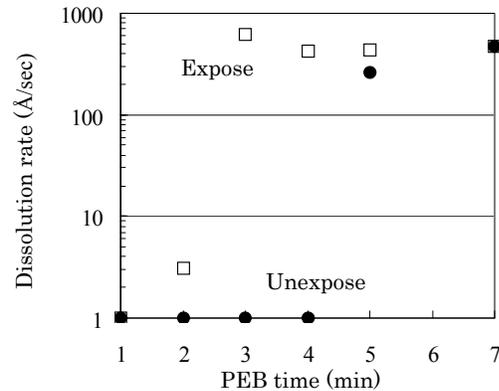


Figure 8. Effect of PEB time on dissolution rate for PHA/*t*-Boc BHF/ITS/dissolution rate for PHA/*t*-Boc BHF/ITS/PTMA (73/18/7.5/1.5 wt/wt/wt/wt) resist system in exposed (□) and unexposed (●) areas. The *i*-line exposure and PEB temperature were fixed at 100 mJ/cm² and 120 °C, respectively.

Based on the studies involving PTMA loadings, and PEB temperature and time, a PSPBO consisting of PHA (73 wt%), *t*-Boc BHF (18 wt%), ITS (7.5 wt%), and PTMA (1.5 wt%) was formulated. The photosensitivity curve of resist films 1.2 μm thick is shown in Figure 9. The resist containing *t*-Boc BHF and ITS possessed outstanding sensitivity (D_0) of 33 mJ/cm², and good contrast (γ) of 5.1.

Figure 10 shows the scanning electron micrograph of a contact-printed image obtained with the system described: the resist layer was exposed to 50 mJ/cm², post-baked at 115°C for 3 min, and developed with 2.38wt% TMAHaq/2.5wt% *i*PrOH at 25°C. A clear, positive pattern with an 3-μm feature was observed using a 3-μm thick film.

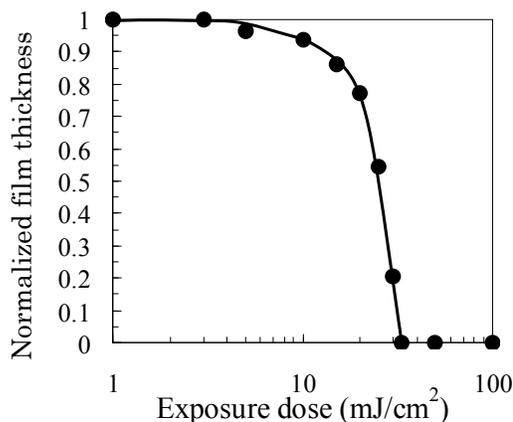


Figure 9. Characteristic photosensitive curve for the PHA/*t*-Boc BHF/ITS/PTMA (73/18/7.5/1.5 wt/wt/wt) resist system. The PEB temperature and time were 120°C and 3 min, respectively.

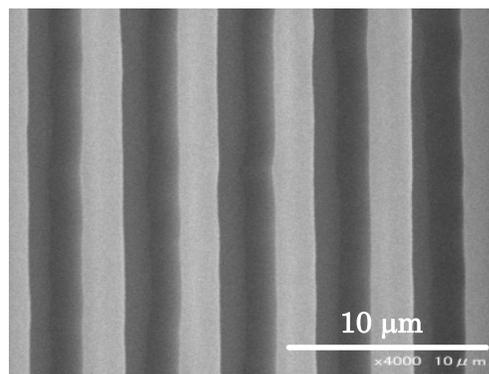


Figure 10. SEM image of positive-pattern 3- μ m-thick film based on PHA/*t*-Boc BHF/ITS/PTMA (70.4/21.1/7.1/1.4 wt/wt/wt/wt).

Low-Temperature Cyclization of PHA.

The printed pattern was converted to a PBO pattern without deformation by heating at temperatures up to 150 °C for 10 min and 250 °C for 20 min under nitrogen. The formation of PBO was confirmed by IR spectroscopy.

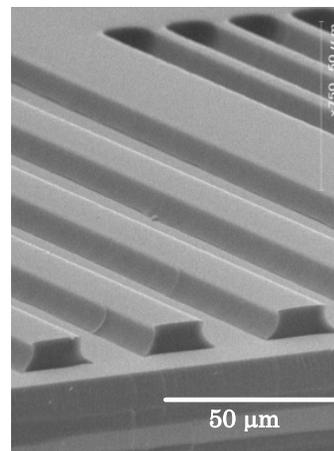
Thick pattern formation

The resist system was used to produce a thick pattern. The 20- μ m image was made in 10- μ m-thick film by PEB at 115°C for 3 min after exposure to 70 mJ/cm² of *i* line, followed by developing with 2.38wt% TMAHaq/2.5wt% *i*-PrOH at 25°C for 110 sec. Adequate resolution and edge sharpness can be seen in Figure 11.

Figure 11. SEM image of positive-pattern 10- μ m-thick film based on PHA/*t*-Boc BHF/ITS/PTMA (70.4/21.1/7.1/1.4 wt/wt/wt/wt).

Summary

Two TAGs (IMS and ITS), which improve the sensitivity and transparency at the *i* line region of PSPBO, and accomplish low-temperature cyclization of PHA to PBO, were prepared from isopropyl alcohol and



methanesulfonyl chloride or *p*-toluenesulfonyl chloride. ITS satisfied the requirements for TAG, and was used for formulation of a positive-type alkaline developable PSPBO based on a PHA, *t*-Boc BHF, and PTMA. The new resist system showed high sensitivity and contrast of 33 mJ/cm² and 5.1, respectively, with *i*-line exposure. Furthermore, the clear positive image after development was converted to a PBO image by low-temperature treatment. A thick pattern also was obtained with the PSPBO system. This new formulation method provides a more efficient and versatile process compared to the standard route that requires large exposure doses and high cyclization temperatures.

References

1. K. Fukukawa, Y. Shibasaki, M. Ueda, *Polym. Adv. Technol.*, **17**, 131 (2006)
2. T. Ogura, K. Yamaguchi, Y. Shibasaki, M. Ueda, *Polym. J.* **39**, 245 (2007)