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SHORT COMMUNICATION

A Negative-Type Photosensitive Poly(3-hexylthiophene) with Cross-Linker and Photoacid Generator

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KEY WORDS: Poly(3-hexylthiophene) / Photosensitivity / Cross-Linker / Photoacid Generator / π-Conjugated Polymer /

π-Conjugated polymers (πCPs) have received great attention for their potential application to electronic devices derived from their semiconductive property.[1] Among them, poly(3-hexylthiophene) (P3HT) is of great interest because of easy preparation, high charge mobility, and high processability. Based on these benefits, P3HT has been used in a wide variety of electronic devices, such as organic solar cells,[2] organic field-effect transistors (OFETs),[3] and sensors.[4]

Generally, a micro-patterned P3HT is fabricated by the microcontact printing (μCP) method with a poly(dimethylsiloxane) stamp.[5] However, this method requires complicated operation resulting in low productivity. To overcome this problem, direct patterning onto polythiophenes based on a photolithographic method is highly required. Direct patterning onto P3HT was demonstrated when an exposed area became insoluble due to cross-linking of an alkyl chain under irradiation with UV light.[6–8] However, the cross-linking of P3HT by irradiation required a huge exposure dose. Recently, efficient patterning methods of polythiophene derivatives were reported.[9–11] These methods require multi-step reactions for the preparation of matrix polymers.

In this paper we propose a new, simple patterning process of P3HT by combining hexamethoxymethylmelamine (CYMEL) as a cross-linker and diphenyliodonium-9,10-dimethoxyanthracene-2-sulfonate (DIAS) as a photoacid generator (PAG). The structures of the chemicals are shown in Figure 1. P3HT was easily synthesized by oxidation polymerization and a photosensitive P3HT was prepared from a mixture of each component. In the exposed area, the aromatic rings of P3HT react with a carbocation formed from CYMEL and cross-link with each other in the presence of acids from DIAS by irradiation. This eletrophilic substitution reaction is novel to the best of our knowledge, although the similar reaction based on arylene compounds has been reported.[12] High-resolution patterns of πCPs are expected from this approach.

EXPERIMENTAL

Materials

3-Hexylthiophene (3HT) was obtained from Aldrich and distilled under reduced pressure before use. Iron chloride (III) ($FeCl_3$) was obtained from Wako Pure Chemical Industries, Ltd. Chloroform was dried with $CaCl_2$ and distilled under nitrogen atmosphere before use. Other reagents and solvents were obtained commercially and used as received.

Preparation of P3HT

P3HT was synthesized according to the previous literature.[13] $FeCl_3$ (9.73 g, 60 mmol) was dissolved in 300 mL of chloroform under nitrogen atmosphere. 3HT (2.52 g, 15 mmol) was added to the solution at $-10\,^{\circ}C$, and stirred for 12 h. The reaction mixture was poured into methanol/hydrochloric acid (90/10 v/v) mixture and the precipitate was collected. The chloroform solution of P3HT was poured into methanol with KOH (10 wt %), and the dark purple precipitate was collected and dried. The yield was 2.2 g (87%).

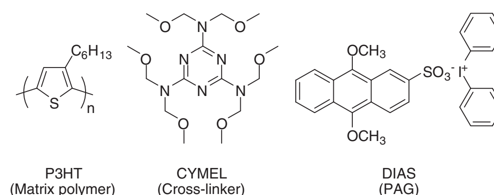

Figure 1. Structures of P3HT, CYMEL, and DIAS.

Dissolution Rate

P3HT was dissolved in 1,1,2,2-tetrachloroethane, followed by addition of CYMEL (20 wt %) and DIAS (10 wt %) (solid content: 3 wt %). The 100-nm thick polymer films were obtained by spin-casting from the solution on a silicon wafer. These films were pre-baked at $80\,^{\circ}C$ for 3 min, and then exposed by non-filtered ultra-high pressure mercury lamp, followed by post-exposure baked (PEB) at temperature (140–180 °C) for 5 min. The dissolution rate (Å/s) of the film thickness was determined from the changes in the film thickness before and after development with tetrahydrofuran (THF).

RESULTS AND DISCUSSION

P3HT, used as the matrix polymer, was synthesized by oxidation polymerization with $FeCl_3$ in chloroform. The M_n and M_w of P3HT were determined to be 31,100 and 71,800, respectively by gel permeation chromatography with a polystyrene standard. The head-to-tail regioregularity was calculated to be 85% by an integral ratio from 2.81 and 2.56 ppm peaks assignable to methylene protons next to thiophene rings in the ^1H NMR spectrum.[13]

The UV-visible absorption spectra of P3HT films with and without DIAS (20 wt %) are shown in Figure 2. The absorption of P3HT/DIAS film increased in the range of 300–450 nm because of the absorption of DIAS.

To investigate the dissolution behavior of the exposed and unexposed areas, the effects of the PEB temperature and PEB time on the dissolution rate were studied. The dissolution rate of the exposed and unexposed areas in several PEB temperatures is shown in Figure 3. The dissolution rate in the exposed area decreases with increasing the PEB temperature. On the other hand, it is almost the same in the unexposed area. The dissolution contrast (DC) between the exposed and unexposed areas reaches about 10 times after PEB at $180\,^{\circ}C$ for 5 min. This result indicates that the cross-linking reaction is promoted effectively by high PEB temperature.

The effect of the CYMEL loading on the dissolution rate was studied, and the results are shown in Figure 4. The dissolution rates of the exposed area slightly decreased with increasing CYMEL content. The DC between

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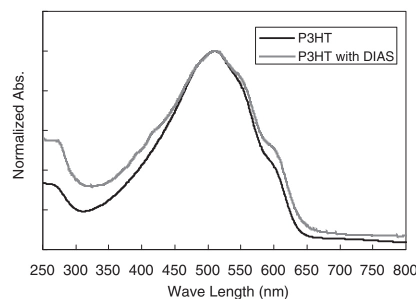

Figure 2. UV-vis absorption spectra of P3HT (solid line) and P3HT with DIAS (dotted line).

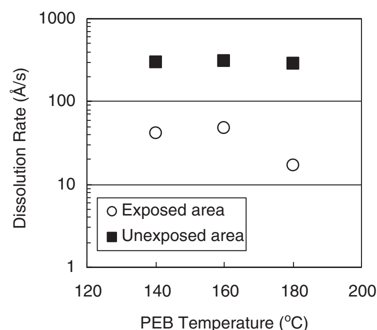

Figure 3. Effect of PEB temperature on the dissolution rate for the P3HT film (P3HT/CYMEL/DIAS: 70/20/10 wt %) in the exposed (○) and unexposed areas (■). Both the non-filter exposure time and PEB time were fixed at 5 min, and THF was used as the developer.

the exposed and unexposed area changes from 5 to 10 times with increasing CYMEL content.

To clarify the effects of CYMEL and DIAS, photo-irradiation of pure P3HT film was carried out. The exposed area was dissolved completely in THF by non-filter UV exposure for 5 min and became insoluble in THF after irradiation for 30 min. On the other hand, the DC of P3HT film with CYMEL and DIAS was obtained under non-filter UV exposure for 60 s. These results clearly indicate that this direct patterning method of P3HT was superior to previous methods using cross-linking reactions of the alkyl chain.

Figure 5 shows an optical image of the contact-printed pattern obtained with the resist system described above. The resist film composed of P3HT (70 wt %), CYMEL (20 wt %), and DIAS (10 wt %) was post-baked at 180 °C for 5 min after exposure, developed with THF, and rinsed with chloroform. Consequently, a clear negative pattern was clearly obtained with 4-µm features on 100-nm thick film.

The conductivity of the patterned P3HT was determined to be $3.3 \times 10^{-5}\,S\,m^{-1}$ at an undoped state and was comparable to that of a pristine P3HT film.[14] Doping of the patterned P3HT with iodine would exponentially increase its conductivity.

CONCLUSION

A novel patterning method of πCPs involving chemically amplified photoresist based on P3HT, CYMEL as a cross-linker, and DIAS as a PAG has been developed. The clear negative pattern with 4-µm features was obtained on the 100-nm thick film consisting of P3HT (70 wt %), CYMEL (20 wt %), and DIAS (10 wt %). This method will be applied to patterning other πCPs.

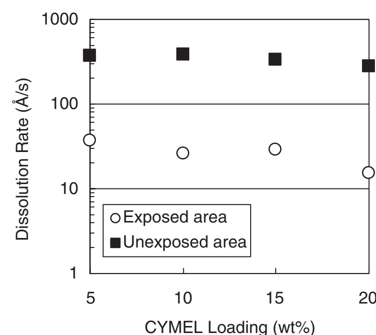

Figure 4. Effect of CYMEL loading on PEB at 180 °C for 5 min on the dissolution rate for the P3HT film (DIAS: 10 wt %) in the exposed (○) and unexposed areas (■). The non-filter exposure time was fixed at 5 min and THF was used as the developer.

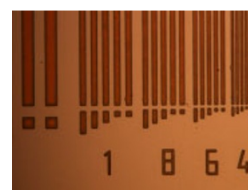

Figure 5. Optical image of patterned P3HT.

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