

# Luminous polyimide bearing the coumarin 6 chromophore in the side group: Synthesis and fluorescence image patterning

Byung-Sik Park\*, Woo Yeon Kim\*\*, and Keun-Byoung Yoon\*\*†

\*Department of Pharmaceutical Engineering, International University of Korea, Jinju 660-759, Korea

\*\*Department of Polymer Science, Kyungpook National University, Daegu 702-701, Korea

(Received 16 August 2013 • accepted 11 October 2013)

**Abstract**—Coumarin was reacted with polyamic acid to form a luminous polyimide that is highly soluble in organic solvents and displays good thermal stability. Luminous side-chain coumarin 6 polyimide was obtained from incorporation of sulfonated coumarin 6 into polyamic acid. This polymer appeared in reddish brown solids and unusually exhibited a fairly strong visible light-emission of a yellowish green color. Fluorescence image patterning of side-chain coumarin 6 polyimide was successfully conducted by microtransfer molding of the polyamic acid and the subsequent thermal treatment for imidization. The polyimides exhibit high fluorescence, opening the possibility of new applications for these polymers.

**Keywords:** Polyimide, Coumarin 6, Fluorescence Image Patterning

## INTRODUCTION

Polyimides are important organic materials in the manufacturing of electronic devices because of their low dielectric constants, low coefficient of thermal expansion and high radiation resistance. These excellent physical properties result from rigid polymer structures and strong intermolecular interactions.

Coumarin and its derivatives have been widely used as a dye for applications in organic electroluminescent diodes (OLED) [1,2], fluorescent probes [3], etc. Polyimides have various outstanding characteristics which make them potential thermostable materials for electronic applications. Coumarin-containing polymers combining the photophysical properties of coumarin and the processing ability of polymers perhaps could also be used in the application fields mentioned above.

The incorporation of chromophore into polyimides has been mainly done by mixing the chromophore with a polymer solution [4-7]. This approach has the disadvantage that a high concentration of chromophore can produce crystallization, phase separation or concentration gradients. Thus, a very convenient approach to avoid the above problems is attaching the chromophore to a polyimide backbone via a single linking group [8,9].

In this work, coumarin 6 was incorporated with side-chain polyimides, coumarin was reacted with a polyimide containing hydroxyl group for optical application of a layer material. The resulting polymer was characterized and its thermal and photophysical properties examined. A significant advantage of this approach is that a great variety of chromophores can be introduced into polyimide through the incorporation of coumarin 6 as side groups.

Fluorescence image patterning of the side-chain coumarin 6 polyimide is also reported by microtransfer molding and the subsequent

thermal imidization. The polyamic acid was well filled in the channel of the PDMS mold and was efficiently transferred to provide a micro-pattern. In this paper, we describe the details of the synthesis of side-chain coumarin 6 polyimide and also the microscopic and spectroscopic characteristic of the resulting microstructures.

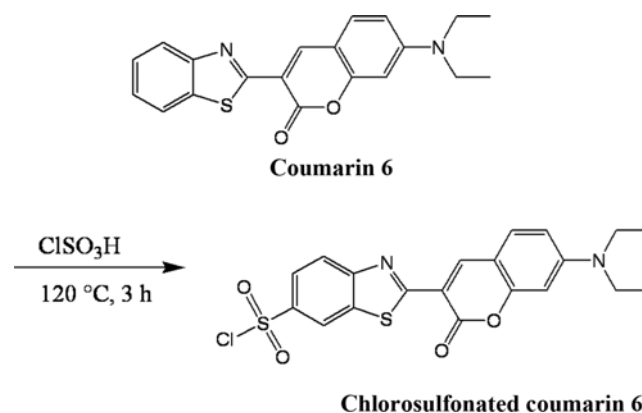
## EXPERIMENTAL

### 1. Materials

2,2-Bis-(3-amino-4-hydroxyphenyl)hexafluoropropane (BAPAF, TCI, Japan) and pyromellitic dianhydride (PDMA, Aldrich, USA) were sublimated at 245 °C under vacuum. 3-(2-Benzothiazolyl)-*N,N*-diethylumbelliferylamine (coumarin 6), triphenylphosphine (PPh<sub>3</sub>) and diethylazodicarboxylate (DEAD) were used as received from Aldrich. *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc) and tetrahydrofuran (THF) were used after fractional distillation.

### 2. Synthesis of Chlorosulfonated Coumarin 6

A mixture of coumarin 6 (1 g, 2.85 mmol) and chlorosulfonic



**Scheme 1.** Synthesis of chlorosulfonated coumarin 6.

†To whom correspondence should be addressed.

E-mail: kbyoon@knu.ac.kr

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acid (8 g, 68.7 mmol) was stirred at 120 °C for 3hrs under a nitrogen atmosphere. After cooling, ice water was added to precipitate and the solid was filtered and washed with several portions of ice water. The product was purified with column chromatography on silica gel (Scheme 1).

### 3. Synthesis of Poly(amic acid)

The synthesis of polyimide is used to illustrate the general synthetic route. A stoichiometric amount of dianhydride (PMDA, 1.635 g, 7.50 mmol) was added to a solution of diamine (BAPAF, 2.745 g, 7.50 mmol) in NMP (30 ml) at 0 °C. Then, the solution was warmed to room temperature and stirred overnight under a nitrogen atmosphere to form the poly(amic acid) (PAA). The viscosity of the solution greatly increased during this period. The obtained polymer solution was poured slowly into 500 ml of stirred methanol, washed thoroughly with methanol and dried under vacuum at 80 °C. The obtained coumarin 6-PAA had inherent viscosity of 1.57 dL/g.

### 4. Incorporation of Coumarin into Poly(amic acid) and Imidization

292 mg of PAA (0.50 mmol), 393 mg of  $\text{PPh}_3$  (1.50 mmol) and 494 mg of chlorosulfonated coumarin 6 (1.10 mmol) were dissolved in dry THF (15 ml) in a flask fitted with a funnel drop, magnetic stirrer and nitrogen inlet. After the PAA was dissolved, 260 mg of DEAD (1.50 mmol) was added dropwise to the solution and stirred at room temperature for 48 hrs. The solution was filtered and the filtered solution poured into an agitated solution of methanol (300 ml) and 2 N HCl (5 ml). The obtained polymer was washed with boiling methanol in a Soxhlet unit and dried in a vacuum at 80 °C.

500 mg of coumarin 6 incorporated PAA (coumarin 6-PAA) was

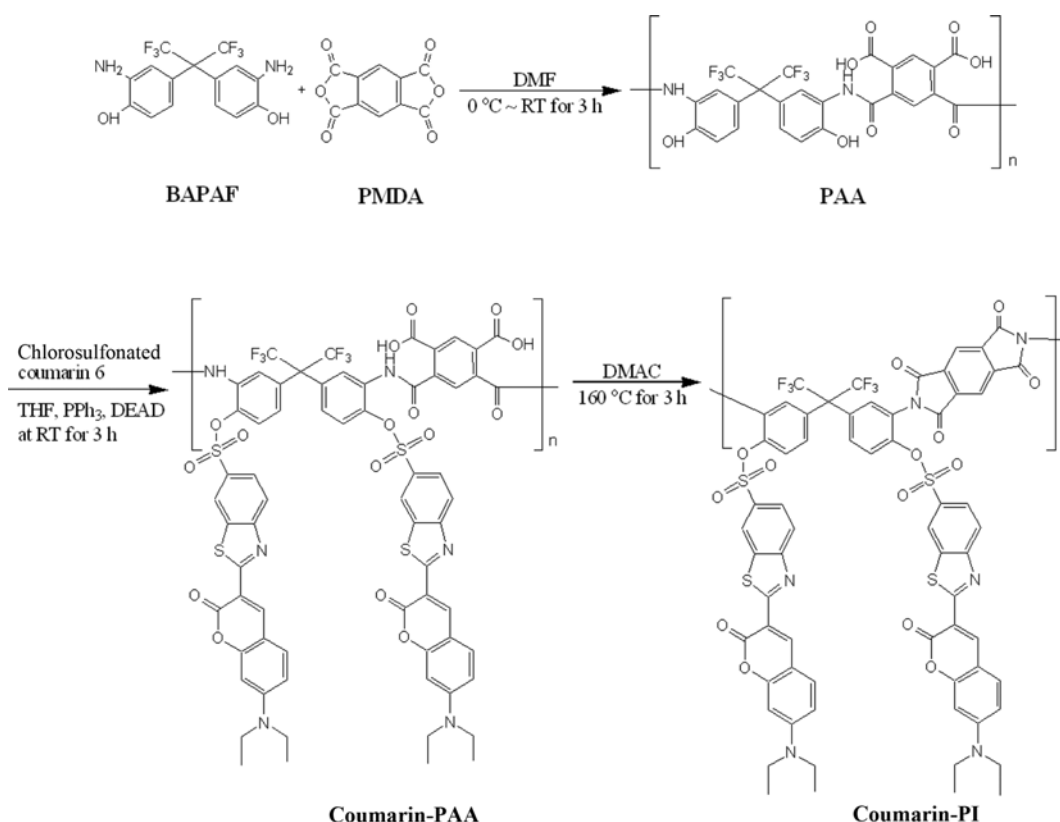
dissolved in dry DMAc (5 ml) and thermally imidized at 160 °C for 3 hrs. The resulting solution was added dropwise into an agitated solution of methanol (100 ml) and 2 N HCl (2 ml). After drying under vacuum at 80 °C for 24 hrs, side-chain coumarin 6 polyimide (coumarin 6-PI) was obtained as a brownish powder. The obtained molecular weight of PAA and the content of coumarin 6 were incorporated with PAA as mentioned previously, the molecular weight of coumarin 6-PI can be estimated approximately.

### 5. Microtransfer Molding [10]

A two-component elastomeric kit (Sylgard 184, Dow Corning) was used to prepare a PDMS mold with the standard mixing ratio of base and hardner, 10 : 1 by weight. The mixture was poured on the master pattern and cured at 80 °C for 20 min. The solidified PDMS mold was contacted to a glass surface and then the polyamic acid solution was dropped in front of a patterned area on the PDMS mold and filled by capillary pressure. The coumarin 6-PAA was solidified by imidization at 160 °C for 3 hrs. Then, the micropattern remained on the glass after removal of the PDMS mold. Finally, the fluorescent image pattern was generated.

### 6. Characterizations

The  $^1\text{H-NMR}$  and IR spectra were recorded on Bruker Avance Digital 400 and Jasco 620V spectrometer, respectively. The UV-vis and PL spectra were measured on UV-2410PC (Shimadzu) and RF-5301PC (Shimadzu) spectrophotometers, respectively. The CCD images were recorded on an Axioplan 2 imaging fluorescence microscope (Carl Zeiss) equipped with a SP 25 series, digital camera. Intrinsic viscosity was measured by using an Ubbelohde viscometer. Decomposition and glass transition temperature were determined



Scheme 2. Synthesis of coumarin 6-PI.

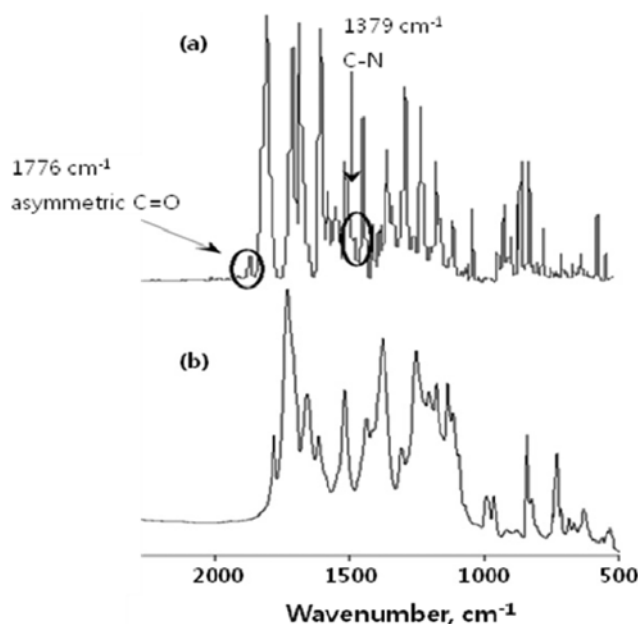


Fig. 1. FT-IR spectra of PAA (a) and coumarin 6-PI (b) (in a KBr pellet).

with TGA (Shimadzu 50 Series) and DSC (Shimadzu 50 Series), respectively. The content of incorporated coumarin 6 was determined with UV-vis calibration curve and TGA.

## RESULTS AND DISCUSSION

A polyimide containing coumarin 6 was synthesized in three major steps: synthesis of soluble poly(amic acid) (PAA), incorporation of functionalized coumarin 6 into PAA as a side group and thermal imidization, in Scheme 2. BAPAF was used as a diamine which contained two hydroxyl groups, to incorporate coumarin 6 into PI. BAPAF has been proven as a very convenient monomer for the preparation of soluble PI [11,12].

The obtained PAA, coumarin 6-PAA and coumarin 6-PI were confirmed by FT-IR and NMR spectroscopy. Fig. 1 shows FT-IR spectra of PAA and coumarin 6-PI.

The IR spectrum of PAA showed absorption peaks at 1,727 (C=O stretching band) and 1,660  $\text{cm}^{-1}$  (sec-amide band). However, others were very confusing because the absorption bands of coumarin 6 and coumarin 6-PAA were overlapped. Even though, the characteristic absorptions of imide rings in coumarin 6-PI were very evident at 1,776 (asymmetrical C=O), 1,723 (symmetrical C=O), and 1,379  $\text{cm}^{-1}$  (C-N).

Fig. 2 shows typical  $^1\text{H}$ -NMR spectra of PAA and coumarin 6-PI in deuterated dimethyl sulfoxide ( $\text{DMSO}-d_6$ ), where all the peaks have been readily assigned to the hydrogen atoms of the recurring unit.

The hydroxyl group on BAPAF can be observed as a singlet at 10.6 ppm (Fig. 2(a)). Although the peak of hydroxyl group could hardly be observed in coumarin 6-PAA and -PI, as shown in Fig. 2(b) and (c), The IR spectra of coumarin 6-PAA and -PI showed also a broad peak between 3,600-3,100  $\text{cm}^{-1}$  characteristic of the stretching vibration of the unreacted hydroxyl groups. It indicated that unreacted hydroxyl groups remained on BAPAF moiety after

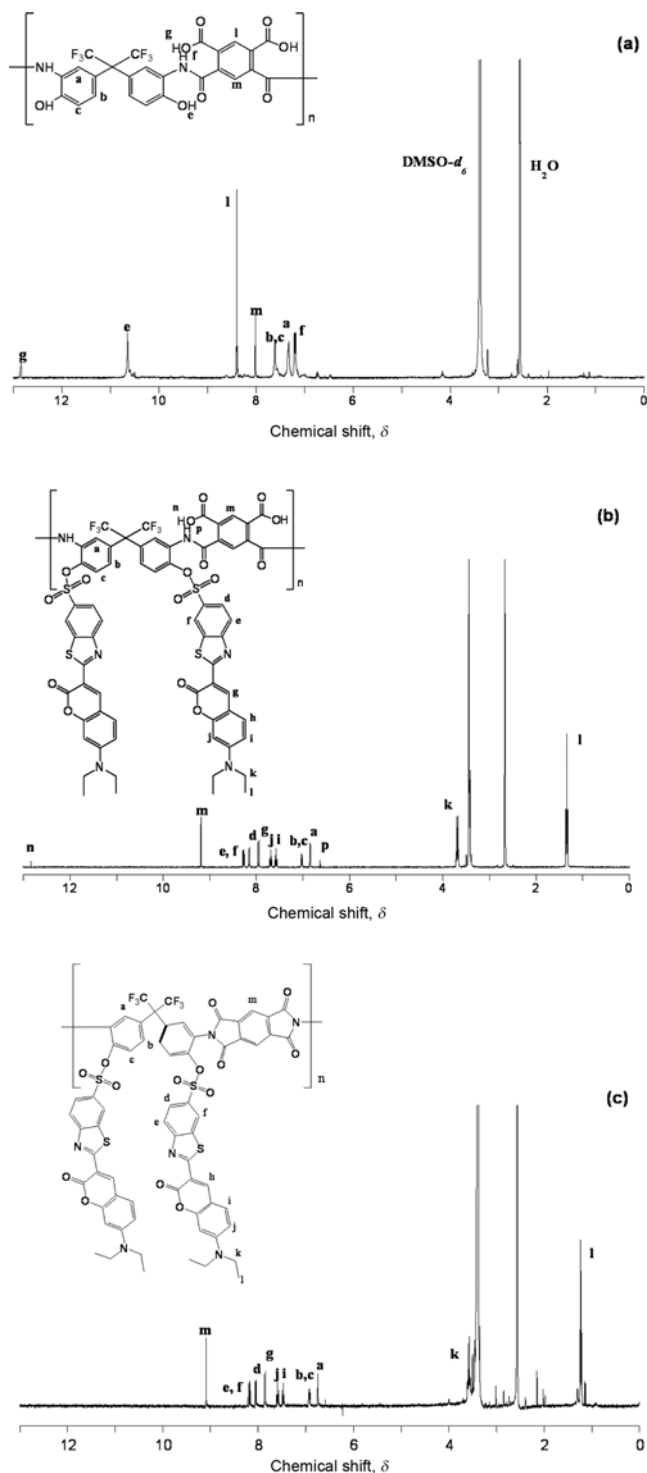


Fig. 2.  $^1\text{H}$ -NMR spectra of PAA (a) and coumarin 6-PAA (b) and -PI (c).

the incorporation of coumarin 6 and thermal imidization. To incorporate the coumarin 6 into PAA, the reaction was carried out using 1.1 equivalents of coumarin 6 per equivalent of hydroxyl group. An estimation of the amount of coumarin 6 incorporated to the PAA could be done using UV-vis spectroscopy by comparing the absorption spectrum of coumarin 6-PAA with solutions. The UV-vis experiments showed that around 23% of coumarin 6 was incorporated

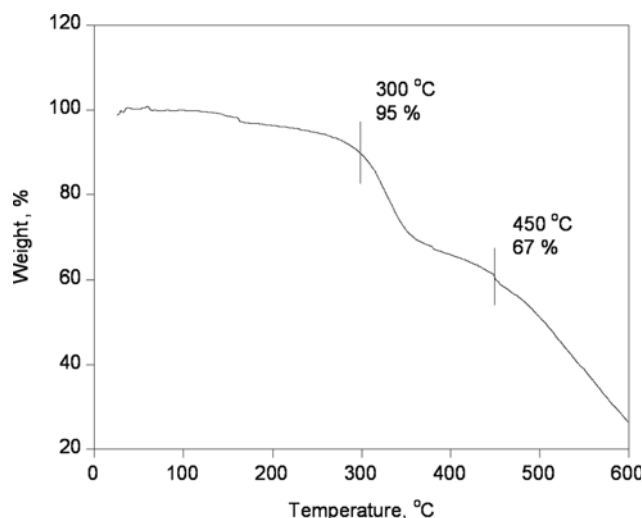


Fig. 3. TGA thermogram of coumarin 6-PI.

into the PAA, and the content of coumarin 6 in coumarin 6-PI was constant after thermal imidization.

TGA analysis gave valuable information about the degree of the polymer modification (Fig. 3). The TGA curve of coumarin-PI showed two degradation steps at 300 and 450 °C. The first step was in the range 300–350 °C and was probably due to the destruction of sulfonate units and coumarin 6 groups, more sensitive to degradation. The second maximum of the decomposition was in the range 450–500 °C and was due to the degradation of the polymer chain itself. The decomposition begins with the scission of sulfonate linkages in coumarin 6-PI. The weight loss after the first degradation steps (28%) corresponded with the theoretical content of the coumarin 6 pendant groups [13].

The important advantage of the introduction of BAPAF and coumarin 6 into the polyimides is their remarkable solubility, which is very important from a practical point of view. The solubility of coumarin 6-PI was tested in various solvents. Coumarin 6-PI was soluble in polar aprotic solvents like NMP, DMAc and DMF. This polymer was also soluble in less polar solvents like dichloroethane and chloroform. The good solubility can be explained by the presence of a hydroxyl group on BAPAF and the bulky pendent coumarin 6 groups, which created a distance between the macromolecular chains preventing a strong packing of the chains, and consequently the diffusion in a solvent was facilitated [14].

UV-vis absorption and fluorescence spectra of the obtained coumarin 6-PI were measured both in solution and film states. UV-vis and fluorescence spectra of coumarin 6, coumarin 6-PAA and -PI in dilute DMF solution are shown in Fig. 4.

The maximum absorption was observed at 460 nm due to coumarin 6 chromophore in dilute DMF solutions, which perhaps resulted from the fact that the incorporation of coumarin 6 did not affect aromatic moieties of polyimide because of the presence of sulfonate spacer between coumarin 6 and polyimide backbone. Besides that, the absorption peak due to imide group was very weakly observed at around 280 nm. The emission spectra at the excitation wavelength of 460 nm have only one peak at 510 nm; no other fluorescence was detected due to the complete population of the first excited state.

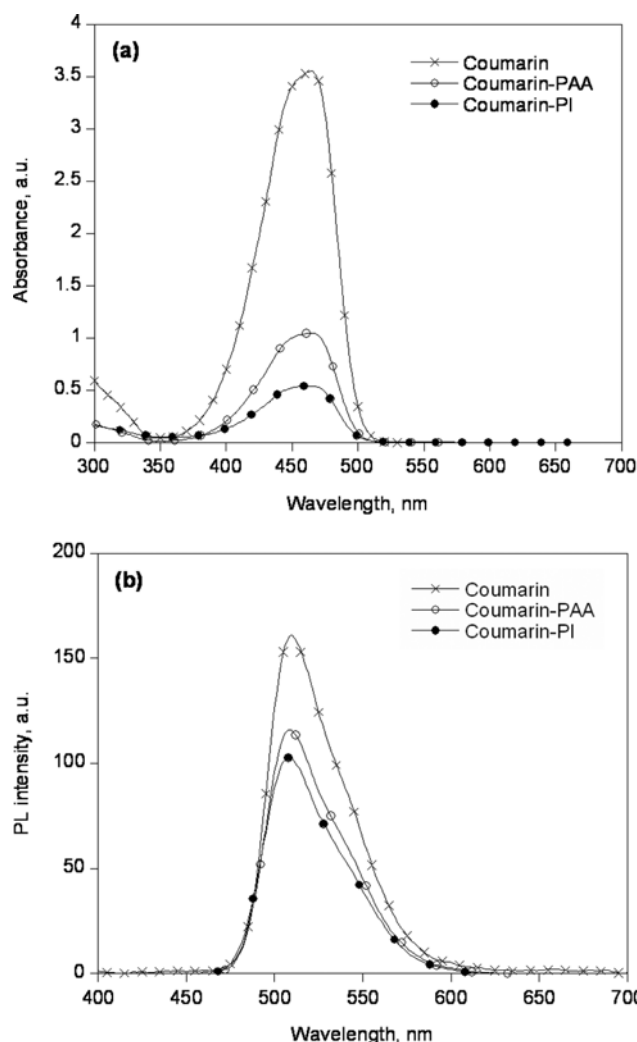


Fig. 4. UV-vis and PL spectra of coumarin 6 and coumarin 6-PAA and -PI ( $\lambda_{\text{ex}}=460$  nm,  $c=1 \times 10^{-6}$  M in DMF).

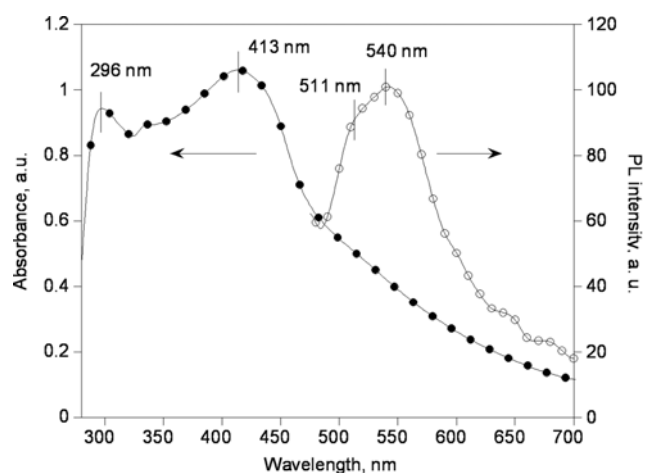


Fig. 5. UV-vis and PL spectra of coumarin 6-PI ( $\lambda_{\text{ex}}=413$  nm).

Fig. 5 shows UV-vis and fluorescence spectra measured in the film state of coumarin 6-PI. The UV-vis spectrum exhibited two major absorptions at 296 and 413 nm, differently from that meas-

ured in a solution state. The former originates in  $\pi \rightarrow \pi^*$  transitions of the partially conjugated double bonds due to the nitrogen atom of the imide moiety, and latter is due to the coumarin 6 chromophore in the side group. The result in the film state may originate from the presence of relatively strong intra- and intermolecular interactions, different from that in dilute solution.

The emission band of coumarin 6-PI was considerably shifted to a long wavelength, and emission occurred in a broad range from 450 to 600 nm in a film state. The emission of coumarin 6-PI consists of two wavelengths due to the excited coumarin 6 and an excimer in its film state. The excimer emission is considered to result from a partially overlapped conformation of coumarin 6 pendant groups. The content of coumarin 6 in coumarin 6-PI was 25 mol%, enough to conform the overlapping of coumarin 6. Since the excimer formation is dependent on the interaction of the neighboring coumarin 6 in an excited state, it is promoted by high incorporation of coumarin 6 into the side-chain of PI. Cheng [15] reported that a higher content of coumarin incorporated with a polymer chain caused a decrease in the emission intensity and induced a red-shift of the maximum absorption wavelength of the coumarin chromophore due to the excimer formation caused by the enhanced interaction between coumarin molecules. The phenomenon is called concentration quenching [16]. In a high concentrated film state, intra- and interchain interaction of coumarin moieties occur more actively than in a dilute solution because of chain packing in the film state. Thus as shown in Fig. 5, emission intensity of coumarin 6-PI film decreased and its emission band was shifted to longer wavelength, compared with that of coumarin 6-PAA film, which the spacer between coumarin 6 incorporated with polymer chain is relatively wide, as well as that in solution state.

Fluorescence image patterning of coumarin 6-PAA was conducted by a microtransfer molding process. Fig. 6 shows the optical- and fluorescence microscope images of the multichannels after thermal imidization.

Fluorescence image patterning has been conducted exclusively by a typical photolithographic method in several research groups [17,18]. Meanwhile, a microtransfer molding process is usually fast and inexpensive as compared to the photolithographic technique, which can be easily adopted for patterning non-planar surfaces and three-dimensional structures. Recently, new approaches for fabricat-

ing multilayered dimensional microstructures have been reported as promising alternatives to conventional photolithography technique [19,20].

As shown in Fig. 6(a), it is certified that relatively clear and smooth patterns were formed without any residue on the glass surface. Additionally, the obtained image patterns appeared in relatively strong visible fluorescence of yellowish green color when exposed to 480 nm UV-visible light amplified by an objective lens under a fluorescence microscope (Fig. 6(b)).

## CONCLUSIONS

We successfully synthesized a luminous polyimide bearing the coumarin 6 chromophore in the side group. The polyimide has good solubility even in less polar solvents such as dichloroethane and chloroform as well as a high thermal stability. Besides, the polymer exhibits an unusual UV-vis absorption in a wide range and a relatively strong visible emission of yellowish green color. With microtransfer molding of the coumarin 6-PAA, image patterns in 3-dimensions of coumarin 6-PI were obtained without leaving any residual layer on the glass surface. Now, we are pursuing the study with the present polyimides to the applications as a layer material for optical devices. Moreover, the polyimides exhibit high fluorescence opening the possibility of new applications for these polymers.

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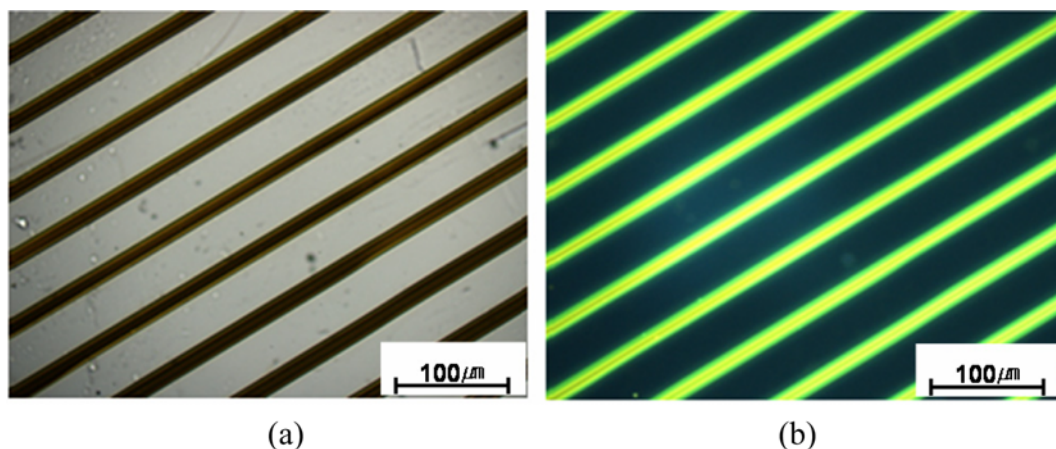


Fig. 6. Optical- and fluorescence microscope images of multichannels after thermal imidization (15×15 μm, width and height).

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