

Chemo-fluorescent Patterning on Flexible Sulfide-Containing Polyimides Film

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Aromatic polyimides (PIs) are promising high-performance materials, due to their outstanding thermal and dimensional stability, high chemical resistance, good mechanical strength and easy film formation. They are being extensively used in microelectronics, photonics, optics, and aerospace industries. There are significant achievements of the fundamental research for improving their properties by modifying the chain backbones and introducing functional groups into the polymer structure. Among them, the photophysics, photochemistry, and optical properties of polyimides have been intensively studied¹. It is well known that the charge-transfer (CT) interactions caused by the donor-acceptor chain sequence act a crucial role in the optical behaviors of PIs. Lots of work has been done in suppressing the intra- and inter-molecular CT interaction for developing a PI film with lighter color or even colorlessness. Recently, we also found that by controlling the intensity of CT interactions, the polyimides film could exhibit wholly different photoluminescence behavior. The CT-inhibited PI had a tendency to possess a higher fluorescence intensity².

In this work, we made a further attempt in modulating the CT intensity by the displacement of the diamine moieties from a donor to an acceptor via a simple oxidation reaction.

The polyimide with a strong donor group diphenyl sulfide in the diamine moiety is shown in **Figure 1**, which was fabricated into flexible film after a conventional two-step thermal imidization process on a clean dry glass plate. This golden yellow polyimide film exhibited non-fluorescent property under the irradiation of 365 nm UV lamp. This was analogous to the traditional aromatic polyimides which are suffered from the intense CT interaction originated from the diamine donor moieties to the dianhydride acceptor moieties, leading to the quenching of fluorescence.

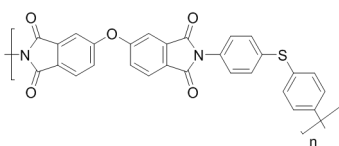


Figure 1 The structure of sulfide containing polyimide.

However, when immersed in a H₂O₂/acetic acid (HAc) (5:1) warm mixed solution for 2 hours, the polyimide film showed a greenish fluorescence under the irradiation of 365 nm UV lamp. Since H₂O₂/HAc is an oxidant and there is no oxidation site in the polymer unit except for the sulfide group, it is reasonable to assume that the transformation from the non-fluorescence to fluorescence is derived from the oxidation of the sulfide group in the diamine moieties. This presumption was proved by the results of Fourier Transform infrared spectroscopy (FTIR), which is shown in **Figure 2(a)**. The polyimide film had almost the same FTIR spectra before and after the treatment, except for the areas at 1292 cm⁻¹ and 1153 cm⁻¹ pointed out by the shadow, which were corresponding to the asymmetric

S=O stretching and symmetric S=O stretching, respectively. The appearance of the infrared absorption bands of S=O stretching suggests the change of the chemical structure of the polyimide. The differential spectrum (**Figure 2(b)**) for the two FTIR spectra was also made for a more obvious comparison. Besides, the intensity changes of 800~600 cm⁻¹ infrared absorption bands which corresponds to the vibration of phenyl rings, suggested that chemical groups linked to them had been changed, and these groups should be the sulfide moieties.

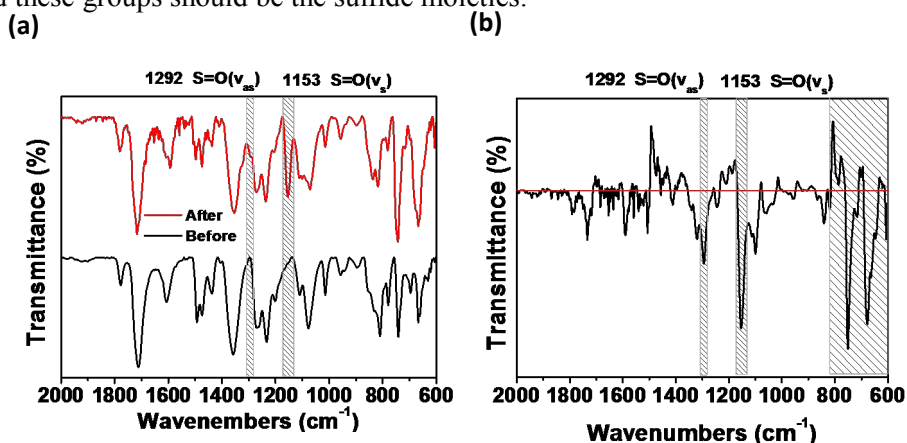


Figure 2 The spectra of (a) FTIR for the sulfide containing polyimide before and after H₂O₂/HAc treatment, and (b) their differential FTIR.

Considering that the oxidation product sulphone or sulfoxide is a typical electron acceptor, the transformation helped alleviate the CT interactions between diamine donor moieties and the dianhydride acceptor moieties, and made contributions to the appearance of fluorescence. To our relief, the film remained highly flexible. Thus, we attempt to apply this process in patterning the film. A letter ‘Z’ was carved on a waxed polyimide film. Then the trench was filled with H₂O₂/HAc mixed solution. After a 2 hours heating in a 60 °C oven, the wax was peeled off, leaving a pure polyimide film, as shown in **Figure 3(a)**. Obvious difference between the patterning area and its outside could not be seen, as shown in **Figure 4**. There was just a little drop of the transmittance of the film detected in the patterning area. However, when irradiated under UV light, the pattern showed obvious fluorescence (**Figure 3(c)**), while the remanent area remained non-fluorescent. Their emission spectra were measured with a fluorescence spectrometer as shown in **Figure 4**. The emission intensity ratio between the fluorescent area and the non-fluorescent ($R_{f/nf}$) at the emission peak of the pattern (537 nm) was up to 12.4. However, one should notice that the back face of the polyimide film also exhibited non-fluorescent property (**Figure 3(b)**), suggesting that the transformation of the chemical structure occurred merely on the surface of the polymer. This helps elucidate the retention of the flexible property after the oxidation treatment.

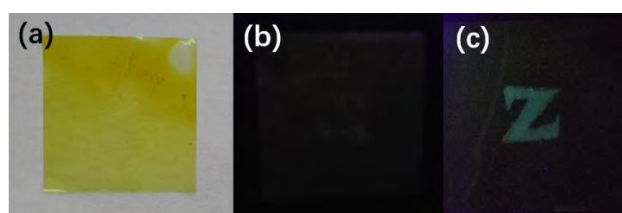


Figure 3 The appearance of polyimide after patterning (a) under ambient light, (b) the back face under UV light and (c) the front face under UV light.

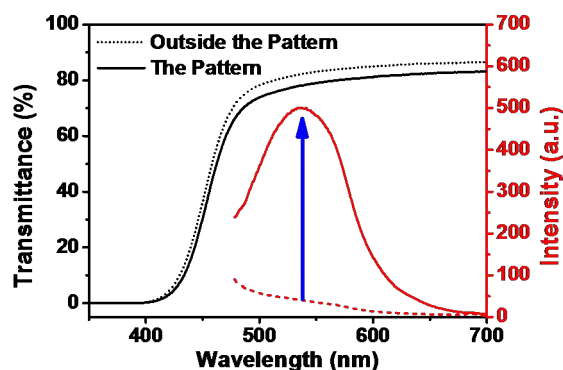


Figure 4 The transmittance spectra (black solid and dotted lines) and the emission spectra (red solid and dotted line, excited at 456 nm) of the pattern and its outside area.

In summary, a wholly aromatic flexible polyimide film was fabricated by the condensation reaction between 4,4-oxydiphthalic anhydride and 4,4'-thiodianiline. This non-fluorescent polyimide film turned into fluorescent material when immersed in a mixed solution of H₂O₂/HAc. It was found that the sulfide group which was characterized by donor property turned into sulphone or sulfoxide during the oxidation process of H₂O₂/HAc, as evidenced by FTIR. The strong CT interactions between the diamine donor moieties and the dianhydride acceptor moieties were thus weakened, resulting in the fluorescence of polyimide without sacrificing the mechanical property. This transformation from non-fluorescence to fluorescence (the $R_{f/nf}$ value up to 12.4) was subsequently applied in patterning on the polyimide film, which showed no obvious visible difference in the area before and after the patterning. This chemo-fluorescent painting as well as the flexible and high thermal stable characteristics of the polyimide film indicated its potential use in the field of high-performance anti-counterfeit materials.

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