Orientation Control of Fluorine-Containing Fluorescent Polyimides using Liquid Crystalline Precursor and Polarization Character of Fluorescent Emission

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Aromatic polyimides (PIs) have been attracting much interests due to the potential applications as novel fluorescent (FL) materials bearing high durability. We have previously reported that an aromatic PI with bulky side groups in the diamine moiety exhibited FL emission, in which the C-N aromatic imide bond was twisted by the steric hindrance, and the locally excited (LE) state with FL emission became dominant, whereas, in typical aromatic PIs, charge transfer (CT) excited state without FL ability is dominant. In this study we focused on a PI precursor, poly (amic ethyle ester)s (PAEs), exhibiting liquid crystal phase in NMP solution (**Fig. 1**) and polarized fluorescence can be generated through the orientation induced in the LC phase. We designed novel PAEs and discussed the relationship between the degree of chain orientation order and the polarizability of fluorescent emission in the PAE and resultant PI film.

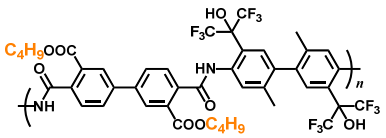

Fig. 1 Chemical structure of PAE precursor for aromatic PI exhibiting fluorescent emission.

Uniaxially oriented PI films were prepared by coating of 60 wt% NMP solution of PAE on Si wafer by applying shear deformation and subsequently heated up to 350 °C by 10 °C/min. Uniaxial orientation order parameter, $S = (3\langle\cos^2\theta\rangle - 1)/2$, where θ is the angle between molecular axis and averaged orientation direction, was evaluated by polarized FT-IR measurement. In the case of spin-coated films, S values 0, and 1 correspond to random, and perfect uniaxial orientations, respectively. The degree of orientations of PAE was as high as 0.5, and the orientation order was gradually decreased during thermal curing accompanying the solvent evaporation and imidization because thermally activated molecular motions can relax the orientation. Anisotropy of fluorescence was analyzed by a polarized fluorescence microscope. In this measurement, non-polarized excitation light was irradiated on the oriented sample, and a polarization analyzer was rotated to estimate the degree of polarization of the FL emission. As shown in **Fig. 2**, the oriented PAE films exhibited the strongest fluorescence when the transmission direction of analyzer was parallel to the orientation direction. Consequently, we have successfully prepared uniaxially oriented PI films which emit linearly polarized fluorescence through lyotropic liquid crystalline state of the PAE precursor.

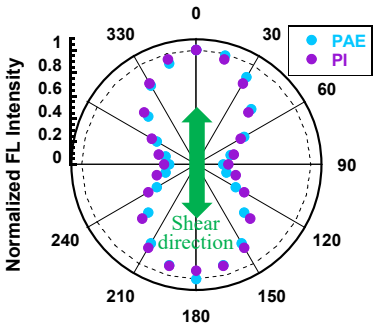

Fig. 2 Polar diagram of polarized fluorescence intensity for cross linked films.

Keywords: Fluorescent polyimide, Liquid crystal, polarized fluorescence emission.