Development of porous polybenzoxazole for low dielectric constant materials

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Introduction: Considerable effort has been made to develop low-dielectric constant (low-*k*) materials for buffer coating. Polybenzoxazole (PBOs) have emerged as a substituent of polyimide due to their intrinsic lower *k* values and moisture absorption ability than those of the polyimides. However, the very limited solubility in solvents only allows fiber fabrications, and the film formation from PBO is rather difficult. Our strategy for the development of a processable PBO having a very low *k* value is to functionalize the PBO precursor with *tert*-butoxycarbonyl (t-Boc) groups and utilize the t-Boc-functionalized PBO precursor (t-Boc prePBO: **Fig. 1**) for a film fabrication [**1**].

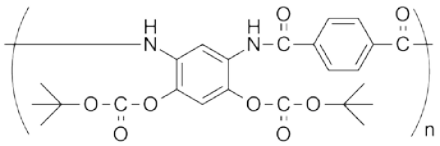

Fig. 1 Chemical Structure of PBO precursor (t-Boc prePBO).

Experiments: t-Boc prePBO was synthesized by polycondensation of 4, 6-di(trimethylsilylamino)-1,3-di(trimethylsiloxy) benzene and Terephthalic acid in *N*-methylpyrrolidone (NMP), followed by adding triethylamine and di-*tert*-buthoxy carbonate to the polymer solutions. The resulting polymer solution was poured into diethylether and dried at room temperature under vacuum.

Results and discussion: We successfully synthesized t-Boc prePBO showing an excellent solubility in the common organic solvents such as *N*,*N*-dimethylacetamide, NMP and fabricated free-standing PBO film from the PBO precursor film by a thermal treatment. The *k* value of the PBO film at 1 MHz was calculated based on the capacitance measured by an impedance gain phase analyzer. Interestingly, the film showed a remarkable low *k* value (k = 2.37), which is much lower than that of PBO fiber (Zylon®) (k = 3.0). This dramatic low *k* value suggested the formation of pores in the PBO film derived from the decomposition of the t-Boc moiety. SEM observations revealed the formation of a sub-nano (10~100 nm) scale continuous porous structure (**Fig. 2**), which is the first example demonstrating the pore structure in the PBO film by utilizing the t-Boc decomposition.

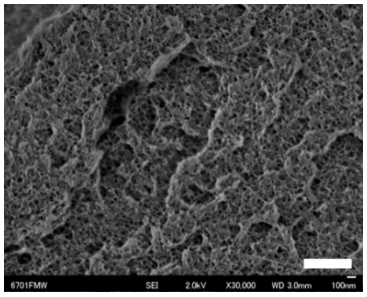

Fig. 2 SEM images of cross-section of PBO films. Scale bars are 500 nm.

Reference

[1] T. Fukumaru, T. Fujigaya, and N. Nakashima, *Polym. Chem.* **2012**, *3*, 369.

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