Development of low-*k* materials based on poly(naphthylene ether)s

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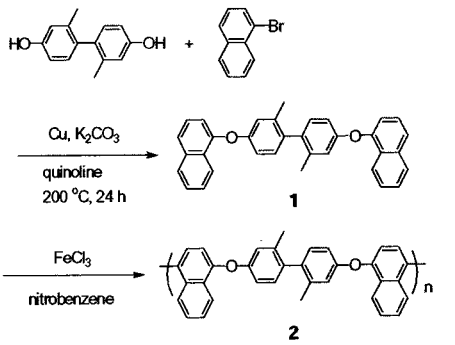
Introduction

Organic polymers have an advantage for low-κ materials because the inherent dielectric constant (ε) values of these materials are relatively lower than that of inorganic materials. However, the low-κ dielectrics require sufficient thermal and mechanical properties to endure the manufacturing process of electric devices, causing the limitation of available polymers for dielectrics only such as poly(imide)s. Recently we have discovered that poly(binaphthylene ether) showed low ε value without sacrificing high thermal stability.[1] This finding may be attributed to its kinked binaphthyl structure involving much free volume to decrease molecular density. Unfortunately, its bulky rigid backbone as well as the low molecular weight rendered the polymer film to be brittle. On the other hand, incorporation of pores in the polymer films, which requires possessing high mechanical strength, can significantly decrease the ε value. Here, we report the synthesis of high molecular weight poly(binaphthylene ether) by oxidative coupling polymerization, and its application to porous films to achieve lower ε value.

Results and discussion

In a previous work, the oxidative coupling polycondensation of binaphthyl ether containing 2,2'-(trifluoromethyl)biphenyl group gave the corresponding high molecular weight polymer enough to make flexible and robust films.[2] Although this polymer showed excellent properties for low-κ dielectrics, incorporation of trifluoromethyl groups is costly undesirable. Therefore, 4,4'-bis(1-naphthyloxy)-2,2'- dimethylbiphenyl (**1**) which is an inexpensive analogue to the fluorine containing monomer was synthesized by Ullmann reaction using 2,2'-dimethyl-4,4'-biphenol and 1-bromonaphthalene. The polymerization of monomer **1** was conducted with 2.5 equiv. of iron (III) chloride as an oxidant in nitrobenzene at room temperature. The white fibrous polymer was obtained with high M_n of 81,000, when the polymerization was carried out for 8 h.



Scheme 1. Synthesis of poly(binaphthylene ether) **2**.

The obtained polymer **2** showed good solubility in such as toluene, tetrahydrofuran and chloroform, and the film obtained from toluene solution was self-standing, transparent and flexible. To the formation of porous film of **2**, the polymer solution with 10 wt% of various porogens in toluene was prepared, then cast to make transparent film that is subject to thermal treatment.

References

1. Tsuchiya, K., Ishii, H., Shibasaki, Y., Ando, S., and Ueda, M., *Macromolecules*, 2004, 37, 4794.
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