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# Synthesis of a Novel Poly(binaphthylene ether) Containing Trifluoromethyl Groups with a Low Dielectric Constant

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## Introduction

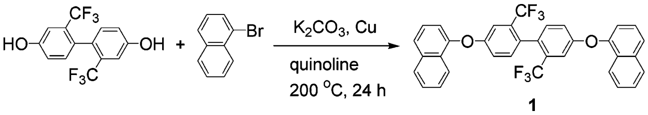
Low dielectric constant (low *k*) insulating materials are required to reduce the resistance−capacitance (*RC*) time delay, cross-talk, and power dissipation in the new generation of high-density integrated circuits.[1] Various low-*k* materials are under investigation, including fluorinated silica glass,[2] amorphous CF,[3] inorganic−organic hybrids,[4] and porous silica materials.[5] A number of polymers with low dielectric constants ($\epsilon$) have been also proposed as insulating materials such as poly(imide)s, poly(aryl ether)s, poly(ether ketone)s, heteroaromatic polymers, and fluoropolymers.[6] Cross-linked poly(naphthylene)s (a cured structure is not clear) derived from cyclopentadienone and acetylene-containing materials are very promising materials with $\epsilon$ of 2.65 at 1 MHz and are commercially available under the name "SiLK".[7,8]

These polymers have a very attractive set of properties; however, a multistep synthesis and high curing temperature (450 °C) is required for these monomers and polymers. A high-temperature curing induces film shrinkage and the poor adhesive strength of the material. Thus, the development of insulation materials prepared by a simple procedure, without sacrificing the low $\epsilon$ of the materials, remains a challenging issue.

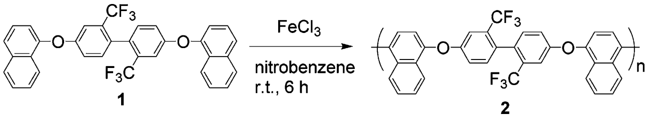
We have recently reported synthesis of poly(2,6-dihydroxy-naphthalene) (PDHN) by catalytic oxidative coupling polymerization, in which the optically estimated $\epsilon$ ($\epsilon_{op}$ at 1 MHz) of the polymer was only 2.56 despite a large number of hydroxyl group on its backbone.[9] We then designed and synthesized a new binaphthalene polymer (PBNE) as the next generation low-*k* material via oxidative coupling polymerization.[10] PBNE shows a high thermal stability (the 5% weight loss = 520 °C and glass transition temperatures = 301 °C), low $\epsilon_{op}$ of 2.59 (at 1 MHz), and better mechanical stability than PDHN. A naphthalene ring is suitable to increase the thermal stability of polymers due to its high chemical bond energy but is not good for decreasing the $\epsilon$ value because of its high molar polarization. The low $\epsilon$ value of PDHN and PBNE may be explained by the large dihedral angle between the neighboring naphthalene rings in its bulky structure that increases the free volume of the polymer, thereby improving the $\epsilon$ value.

Recently, high-temperature low-*k* materials with low dissipation factor (tan $\delta$) are demanded because of the rapid quantitative expansion into the market of electric devices that drive at high frequency over 1 GHz. A large tan $\delta$ material creates an ac leakage current, which converts the dipole motion into heating of the material.

**Scheme 1. Synthesis of Monomer 1**



**Scheme 2. Polymerization of Monomer 1**



On the basis of the background described above coupled with the effectiveness of 2,2′-bis(trifluoromethyl)biphenyl unit for decreasing the $\epsilon$ value while maintaining the thermal stability,[11] we have newly designed and synthesized a high-temperature low-*k* polymer with low tan $\delta$ via oxidative coupling of naphthalene rings. This paper describes the successful synthesis of poly[4,4′-bis(1-naphthyloxy)-2,2′-bis(trifluoromethyl)biphenyl] (**2**) by oxidative coupling polymerization of a novel naphthyloxy monomer 4,4′-bis(1-naphthyloxy)-2,2′-bis(trifluoromethyl)biphenyl (**1**) containing trifluoromethyl groups. The thermal stability, $\epsilon$ value, and tan $\delta$ of **2** are also reported.

## Results and Discussion

**Synthesis of Monomer 1.** It is important to decrease the molecular polarization and molecular density of polymers for the design of low-*k* polymers. Thus, the new monomer **1** having naphthyloxy groups connected by (bistrifluoromethyl)biphenyl with a large dihedral angle between the neighboring phenyl rings and low polarization groups was designed. The characteristic feature of our methodology to development of organic low-*k* materials is that polymerization of **1** yields binaphthyl units in the main chain, which consists of orthogonally bound naphthalene rings. The synthetic route for **1** is outlined in Scheme 1. Monomer **1** was obtained by the Ullmann reaction of 4,4′-dihydroxy-2,2′-bis(trifluoromethyl)biphenyl and 1-bromonaphthalene in quinoline in the presence of copper and potassium carbonate. The product was purified by silica gel column chromatography, followed by recrystallization from hexane to give a white needle.

The structure of **1** was assigned on the basis of elemental analysis as well as IR and $^1$H NMR, and $^{13}$C NMR spectroscopy. The IR spectrum of **1** showed the characteristic absorption corresponding to the C−O stretching at 1234 cm$^{-1}$, and no bands at around 3300−3400 cm$^{-1}$ due to the OH stretching of 4,4′-dihydroxy-2,2′-bis(trifluoromethyl)biphenyl were observed. In the $^{13}$C NMR spectrum, signals assignable to *ortho* and *para* positions of a naphthoxy moiety are observed at 115.2 and 125.0 ppm, respectively, and the other signals were all assigned (see Supporting Information).

**Cyclic Voltammogram.** In the first step of oxidative polymerization, selective one-electron oxidation of the aromatic rings is required. Thus, the oxidation potential of **1** was measured with cyclic voltammetry. The cyclic voltammogram of **1** indicated a clear oxidation peak at 1.55 V. The synthesis of PBNE having the oxidation potential of 1.5 V vs SCE

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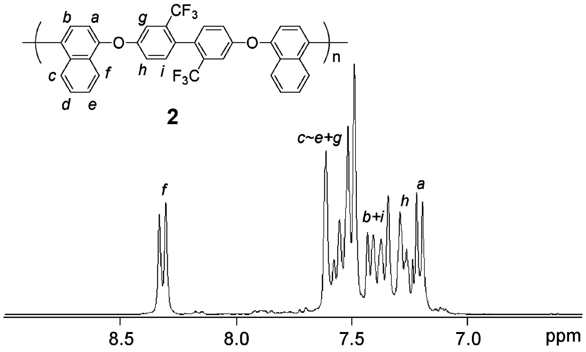

**Figure 1.** Expanded $^{1}$H NMR spectrum of polymer **2**.

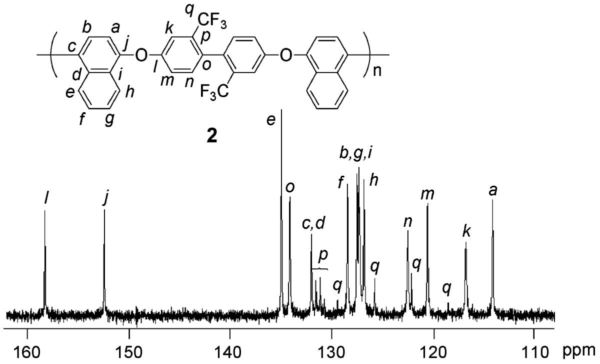

**Figure 2.** Expanded $^{13}$C MNR spectrum of polymer **2**.

proceeded with $FeCl_3$ as an oxidant (see Supporting Information). Thus, $FeCl_3$ was selected as the oxidant for oxidative coupling polymerization of **1**.

**Polymer Synthesis.** Oxidative coupling polymerization of **1** was carried out by using $FeCl_3$ as an oxidant (2.2−2.5 equiv to **1**) at room temperature under a nitrogen atmosphere (Scheme 2). The results are summarized in Table 1. Oxidative coupling polymerization required theoretically 2 equiv of $FeCl_3$ based on the monomer. Although the excess amount of $FeCl_3$ generally increases the rate of the polymerization, unfavorable gelation occurs because of the extra oxidation of polymers. The high-$M_n$ polymer of 32 000 was obtained in 80% (toluene-soluble portion) when the polymerization was carried out using 2.5 equiv of $FeCl_3$ for 6 h. In the synthesis of PBNE, the $M_n$ value was no more than 13 500, mainly because of the hidden coupling point for the polymerization. The monomer **1** was, thus, designed to polymerize more effectively keeping the bulky binaphthalene structure in it, resulting in higher $M_n$.

**Polymer Characterization.** The structure of polymer **2** was characterized by IR, $^{1}$H NMR, and $^{13}$C NMR spectroscopy and elemental analysis. The signal (*c*) at 7.71 ppm due to the *para* position of naphthoxy moiety in **1** disappeared in the $^{1}$H NMR spectrum of **2** (Figure 1). Figure 2 depicts the $^{13}$C NMR spectrum of PNTB, in which signal (*a*) assignable to the *ortho* position of the naphthoxy moiety was observed at 112.7 ppm. In the meantime, the signal (*c*) assignable to the *para* position completely shifted from 125.0 ppm. The signal could not observed because it overlapped with the other signals. In the previous work it was found that the coupling of the naphthoxy group selectively occurred at the *para* position, whose carbon signal shifted from 125.0 to 133.0 ppm.[9] From this finding it is assumed that the signal (*c*) overlaps with the signal (*d*) at 132.0 ppm. These signals completely disappeared in the $^{13}$C-DEPT45 NMR spectrum as shown in Figure 3, indicating the coupling polymerization proceeded dominantly at the *c* position to give a linear soluble polymer. Polymer **2** is a faint yellow solid, soluble in chloroform, toluene, anisole, cyclohexanone, and nitrobenzene at room temperature. A transparent film was cast from a solution of the polymer in toluene.

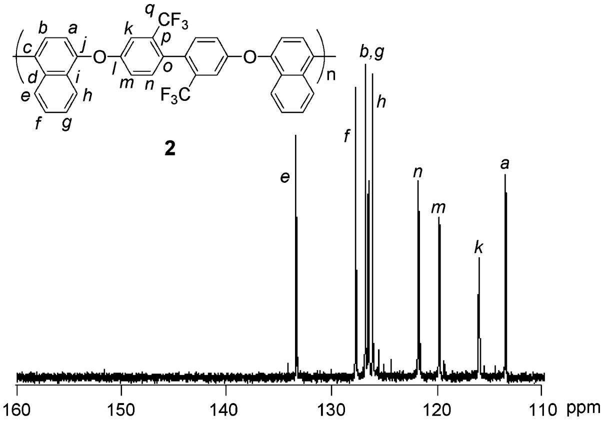

**Figure 3.** Expanded $^{13}$C/DEPT45 NMR spectrum of polymer **2**.

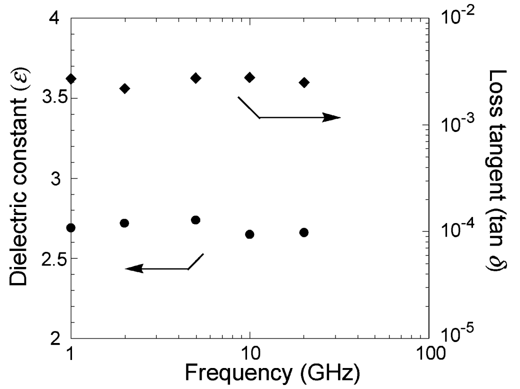

**Figure 4.** Dielectric constants ($\epsilon$) and loss tangents (tan $\delta$) of **2** depending on electric frequency.

The *n* value of **2** was measured at the wavelength of 1.32 $\mu$m using a prism coupler. The in-plane ($n_{TE}$) and out-of-plane ($n_{TM}$) refractive indices are 1.589 and 1.569, respectively. Thus, the birefringence ($\Delta n$) of the polymer is 0.02, smaller than that of PDHN (0.066), which has rigid-rod structure. To realize low tan $\delta$ value, polar groups like imide and hydroxyl moieties should be avoided in the material, and at the same time, the group with high mobility should be eliminated. Polymer **2** fulfills these requirements, and the value is still enough low for the low-*k* material application. The optically estimated $\epsilon_{op}$ at 1 MHz was determined to be 2.50, according to the following equation: $\epsilon_{op} = n^2$. The $\epsilon$ and loss tangent (tan $\delta$) of **2** films were directly measured by the cavity resonance perturbation method[12] in the microwave frequency range (1−20 GHz), in which the sample films were prepared with a thickness of 0.15 mm and a width of 0.52 mm and a length of 80 mm. The results are presented in Figure 4. Increasing the frequency, a small monotonic decrease from 2.7 to 2.65 in $\epsilon$ appears, and the tan $\delta$ values are almost constant as 0.0025 from 1 to 20 GHz. The low $\epsilon$ value is due to the presence of trifluoromethyl groups and voluminous binaphthyl units that increase the free volume of **2**. The tan $\delta$ value of **2** is very small because of its rigid and low polar structure.

The thermal properties of **2** were examined by TG and DSC analysis. The typical traces for **2** are shown in Figure 5. The polymer shows an excellent thermal stability: 5% weight loss temperature ($T_{5d}$) at 530 °C and glass transition temperature ($T_g$) at 230 °C. The $T_{5d}$ value is higher than PDHN (440 °C) and PBNE (521 °C). To improve the thermal property, the cross-

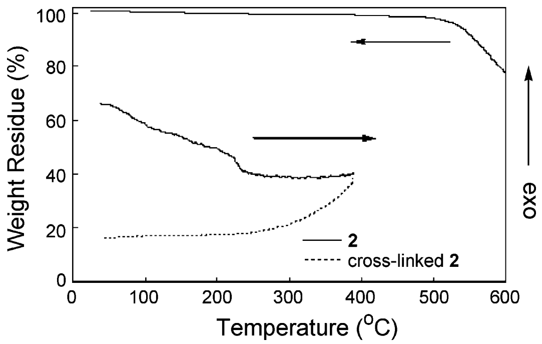

**Figure 5.** TGA and DSC (second scan) traces of polymer **2** (10 °C/min under nitrogen).

**Table 1. Preparation of Polymer 2**

| run | $FeCl_3$ (equiv) | time (h) | yield[b] (%) | $M_n$[c] | $M_w/M_n$[c] |
|---|---|---|---|---|---|
| 1 | 2.2 | 24 | 71 | 6 000 | 2.7 |
| 2 | 2.5 | 6 | 80 | 32 000 | 3.2 |
| 3 | 2.5 | 18 | 54 | 43 000 | 12.3 |

[a] Polymerization was carried out with 0.9 mmol of **1** in 2.8 mL of nitrobenzene at 25 °C under nitrogen. [b] Soluble portion. [c] Determined by GPC eluted with chloroform using polystyrene standard.

**Table 2. Properties of 2 and Reference Polymers**

| properties | 2 | PDHN | PBNE | SiLK[f] |
|---|---|---|---|---|
| $n_{AV}$[a] | 1.582 | 1.600 | 1.613 | 1.629 |
| $\Delta n$[a] | 0.020 | 0.066 | 0.006 | 0.004 |
| $\epsilon_{op}$[b] | 2.50 | 2.56 | 2.59 | 2.65 |
| $\epsilon$[c] | 2.70 | 3.00 | 2.50 | 2.65 |
| tan$\delta$ (20 GHz) | 0.0025 | | | |
| $T_{5d}$[d] (°C) | 530 | 440 | 520 | (450)[g] |
| $T_g$[d] (°C) | 230 (>400)[e] | >400 | 301 | >490 |
| film | flexible | brittle | brittle | |

[a] Average refractive index and birefringence estimated by a prism coupler at a wavelength of 633 nm. [b] Optically estimated dielectric constant at 1 MHz according to the following equation: $\epsilon = 1.0 n_{AV}^2$. [c] Determined from the capacitance. [d] Measured by TGA and DSC at a heating rate of 10 and 5 °C/min, respectively. [e] Cross-linked **2**. [f] Quoted from the ref 8. [g] 0.75% weight loss temperature.

linked film was prepared by casting **2** with 5 wt % of oxybis(3,4-dihydroxymethyl)benzene as a cross-linker from cyclohexanone solution, followed by thermal treatment at 200 °C for 1 h under a nitrogen atmosphere. The peak derived from $T_g$ of **2** was completely disappeared at 230 °C, and no peak could be observed under 400 °C in a second heating process of cross-linked film of **2**.

The physical properties of **2** and some reference polymers are summarized in Table 2. Polymer **2** was designed to have low $\epsilon$, tan $\delta$, high thermal stability, and good film property.

As mentioned above, the thermal property of **2** is excellent compared to other polymers, especially when **2** was cross-linked by heating. The $\epsilon_{op}$ value of **2** is the lowest among these polymers, and the directly measured $\epsilon$ value is lower than PDHN and similar to SiLK. This $\epsilon$ value is of a non-cross-linked film of **2**, and the value will not change after cross-linking reaction.[13] To decrease tan $\delta$, polar groups like imide and hydroxyl moieties and high-mobility groups should be eliminated from the structure. PDHN has hydroxyl groups, and PDHN and PBNE are too rigid to make films. In fact, these polymer films are brittle and difficult to prepare an enough thick film to evaluate the tan $\delta$. From these comparison, the polymer film of **2** has an excellent thermal stability, good film property, low $\epsilon$, and tan $\delta$ values, which fulfill the requirement for the next generation low-*k* materials.

## Conclusions

A new polymer **2** was prepared by oxidative coupling polymerization of **1** using $FeCl_3$, which produced polymers with $M_n$ up to 32 000. The structure of **2** was characterized by $^1H$ and $^{13}C$ NMR spectroscopy and was determined to have a 4,4′-linkage. The polymer showed high thermal stability and good film processability. The synthesis of **1** and **2** is easy, and a high-temperature curing is also unnecessary. The polymer has the low refractive index of 1.582, low dielectric constant of 2.70, and low tan $\delta$ of 0.0025 at 20 GHz. This polymer, with its high thermal and mechanical properties as well as its low dielectric constant and tan $\delta$, will be a good insulating material for future generations of microchips.

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**Supporting Information Available:** Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) (a) Treichel, H. *J. Electron. Mater.* **2001**, *30*, 290. (b) Havemann, R. H.; et al. *Mater. Res. Soc. Symp. Proc.* **1998**, *511*, 3. (c) Morgan, M.; et al. *Annu. Rev. Mater. Sci.*. **2000**, *30*, 645. (d) *The International Technology Roadmap for Semiconductors*; Semiconductor Industry Association: San Jose, CA, 2001.
(2) Sullivan, J. P.; Denison, D. R.; Barbour, J. C.; Newcomer, P. P.; Apblett, C. A.; Seager, C. H.; Baca, A. G. *Mater. Res. Soc. Symp. Proc.* **1997**, *443*, 149.
(3) Endo, K. *MRS Bull.* **1997**, *22*, 55.
(4) Miller, R. D.; Hedrick, J. L.; Yoon, D. Y.; Cook, R. P.; Hummel, J. P. *MRS Bull.* **1997**, *22*, 44.
(5) Ting, C. H.; Seidel, T. E. *Mater. Res. Soc. Symp. Proc.* **1995**, *381*, 1.
(6) (a) Maier, G. *Prog. Polym. Sci.* **2001**, *26*, 3. (b) Liaw, D.-J.; Tseng, W.-T. *Macromol. Symp.* **2003**, 351. (c) Goto, K.; Akiie, T.; Inoue, Y.; Matsubara, M. *Macromol. Symp.* **2003**, 321.
(7) Shah, H. V.; Brittain, S. T.; Huang, Q.; Hwu, S. J.; Whitesides, G. M.; Smith, D. W., Jr. *Chem. Mater.* **1999**, *11*, 2623.
(8) Martin, S. J.; Godschalx, J. P.; Mills, M. E.; Shaffer, E. O., II; Townsend, P. H. *Adv. Mater.* **2000**, *12*, 1769.
(9) Sasada, Y.; Shibasaki, Y.; Suzuki, M.; Ueda, M. *Polymer* **2003**, *44*, 355.
(10) Tsuchiya, K.; Ishii, H.; Shibasaki, Y.; Ando, S.; Ueda, M. *Macromolecules* **2004**, *37*, 4794.
(11) (a) Rogers, H. G.; Gaudiana, R. A.; McGowan, C. *J. Polym. Sci., Polym. Chem.* **1985**, *23*, 2669. (b) Harris, F. W.; Hsu, Steve, L. C.; Tso, C. C. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31*, 342.
(12) Miura, T.; Takahashi, T.; Kobayashi, M. Accurate Q-Factor Evaluation by Resonance Curve Method and Its Application to the Cavity Perturbation. *IEICE Trans. Electron.* **1994**, *E77-C*, 900−907.
(13) Tsuchiya, K.; Shibasaki, Y.; Suzuki, M.; Ueda, M. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 2235.

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