Synthesis of a Novel Poly(binaphthylene ether) with a Low Dielectric Constant

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ABSTRACT: A novel thermally stable and low dielectric poly(binaphthylene ether) (**2**) has been developed. Polymer **2** was easily prepared by oxidative coupling polymerization of 2,2′-bis(1-naphthyloxy)-1,1′-binaphthyl (**1**) with $FeCl_3$ as an oxidant. This polymerization produced regiocontrolled polymer **2** with a number-average molecular weight of 14 000 Da and a molecular weight distribution of 3.3. The 5% weight loss and glass transition temperatures of polymer 2 were 520 and 301 °C, respectively. The dielectric constant of polymer **2** at 1 MHz was directly measured from the capacitance as 2.50. The modulus and hardness of polymer **2** were determined as 9.8 and 0.42 GPa.

Introduction

Scaling down integrated circuit (IC) feature sizes has brought tremendous improvement in both performance and miniaturization capabilities over the past few decades; however, the influence of the capacitive resistance of the interconnect array, which causes signal delay in the devices, cannot be disregarded. To avoid this problem, insulating materials with lower dielectric constants (low *k*) are required.[1] A number of polymers with low dielectric constants have been proposed as insulating materials. These polymers include poly(imide)s, poly(aryl ether)s, poly(ether ketone)s, heteroaromatic polymers, and fluoropolymers.[2] Crosslinked poly(naphthalene)s (a cured structure that is not clear) derived from cyclopentadienone and acetylene-containing materials are very promising materials with a dielectric constant (ϵ) of 2.65 at 1 MHz and are commercially available under the name "SiLK".[3,4] 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 *k* of the materials, remains a challenging issue.

Very recently, Swager et al. reported a new low *k* material using the ring-opening olefin metathesis polymerization of a polymer with triptycene units.[5] The bulky structure of the functional groups restricted the rotation by multiple point attachment, yielding high-temperature-stable material, with an ϵ value in the range from 2.59 to 3.35 at 1 kHz when using a nonfluorinated polymer. However, their mechanical properties have not been reported.

A convenient synthesis of poly(2,6-dihydroxy-1,5-naphthylene) (PDHN) by Cu(II)-amine catalyzed oxidative coupling polymerization of 2,6-dihydroxynaphthalene in solutions was reported.[6] The ϵ value of PDHN was 2.56, estimated from the refractive index ($n = 1.60$, $\epsilon = n^2$). Despite the numerous polar hydroxyl groups and carbon−carbon double bonds that contribute to the high molar polarization of 1.64, the ϵ value of PDHN was lower than those of thermally stable aromatic polymers, such as polyimides and poly(benzoxazole)s. This interesting finding may be explained by the large dihedral angle between the neighboring naphthalene rings in its bulky structure. A hydroxy group, however, induces increased water absorption. These findings prompted the development of another thermally stable, low dielectric polymer based on naphthalene ring coupling.

We here report the synthesis and characterization of a novel poly(binaphthylene ether) for the use of a next generation low *k* dielectrics in microelectronics industry.

Experimental Section

Materials. Nitrobenzene was distilled under reduced pressure over calcium hydride and then stored over 4-A molecular sieves. 1,1′-Bi-2-naphthol was prepared by a reported procedure. The other materials were obtained commercially and used as received.

Preparation of 2,2′-(Bis-1-naphthyloxy)-1,1′-binaphthyl (1). To the solution of 1,1′-bi-2-naphthol (1.146 g, 4 mmol) in quinoline (10 mL) and toluene (10 mL) was added potassium carbonate (1.38 g, 10 mmol), and the mixture was heated at 150 °C for 2 h to remove water with a Dean−Stark apparatus. After the formation of the potassium salt, toluene was removed by heating at 130 °C, and the solution was cooled to room temperature. To this suspension were added copper powder (0.026 g, 0.4 mmol) and 1-bromonaphthalene (1.12 mL, 8 mmol), followed by heating the mixture at 200 °C for 24 h under nitrogen atmosphere. After cooling this solution to room temperature, the reaction mixture was extracted with dichloromethane, and washed subsequently with 1 N HCl and 3% NaOH(aq). The solvents were evaporated, and the residual oil was poured into methanol. The precipitate was collected and purified by silica gel column chromatography (toluene/hexane 1/2 in volume ratio), to give a light yellow needlelike crystal from the recrystallization in acetonitrile. The yield was 1.3 g (62%). Mp: 204−205 °C. ^{1}H NMR ($CDCl_3$): $\delta = 6.78$ (d, 2H),

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7.11−7.18 (m, 4H), 7.25 (t, 2H), 7.39−7.58 (m, 10H), 7.78−7.91 (m, 8H). ^{13}C NMR ($CDCl_3$): δ = 113.4, 119.3, 122.2, 122.5, 123.0, 125.0, 125.9, 126.0, 126.2, 126.7, 126.9, 127.0, 127.7, 128.1, 129.9, 130.8, 134.7, 134.9, 153.2, 153.6. IR(KBr): 1238 (C−O), 1573 and 1592 cm^{-1} (Ph-H). Anal. Calcd for $C_{40}H_{26}O_2$: C, 89.19; H, 4.87. Found: C, 89.21; H, 5.17.

Preparation of Poly(2,2′-(bis-1-naphthyloxy)-1,1′-binaphthyl) (2). To the solution of **1** (0.5 g, 0.9 mmol) in nitrobenzene (2.8 mL, 15 wt %) was added iron(III) chloride (0.36 g, 2.25 mmol) under nitrogen atmosphere. The reaction mixture was stirred for 24 h at room temperature and poured into methanol containing a small amount of concentrated HCl. A precipitate was dissolved in nitrobenzene, reprecipitated with methanol, dissolved in chloroform, and poured into acetone. The precipitate was collected and dried at 200 °C for 1 day under the reduced pressure. The white polymer **2** was obtained in quantitative yield. The polymer was characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy and elemental analysis. The yield was 0.49 g (99%). ^{1}H NMR ($CDCl_3$): δ = 7.08−7.23 (m, 16H), 7.51−7.69 (m, 8H), 8.04 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 112.7, 119.6, 122.7, 125.3, 126.1, 126.4, 126.8, 127.0, 128.2, 128.6, 130.3, 131.0, 133.4, 134.5, 134.9, 153.4, 153.6. IR(KBr): 1230 (C−O), 1585 cm^{-1} (Ph-H). Anal. Calcd for $C_{40}H_{26}O_2$: C, 89.19; H, 4.87. Found: C, 89.21; H, 5.17. Anal. Calcd for $C_{40}H_{24}O_2$: C, 89.53; H, 4.51. Found: C, 89.69; H, 4.78.

Measurement. Infrared spectra were recorded on a Horiba FT-720 spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained on a BRUKER DPX-300 spectrometer at 300 and 75 MHz, respectively. Deuterated dimethyl sulfoxide (DMSO-d_6) was used as the solvent with tetramethylsilane as an internal standard. Number- and weight-average molecular weights (M_n and M_w) were determined by a gel permeation chromatograph (GPC) on a Jasco GULLIVER 1500 system equipped with a polystyrene gel column (Plgel 5 mm MIXED-C) eluted with chloroform at a flow rate of 1.0 mL min^{-1} calibrated by standard polystyrene samples. The film was spin-coated on a silicone wafer from the solution of polymer in anisole. The electrical properties were determined after vapor deposition of gold and aluminum with 600 mm diameter on the surface and back of the film by using a network analyzer (Hewlett-Packard 4280A 1 MHz C meter/C−V plotter). This allowed measuring the capacity and the breakdown voltage of the films. The dielectric constant ϵ can be calculated from the capacity using the formula $\epsilon = cd/A\epsilon_0$, where c is the observed capacity, d the film thickness, A the aluminum area, and ϵ_0 the free permittivity. Young's modulus and hardness were determined with a nanoindenter (Hysitron Inc. Triboscope system) according to the reported procedure.[7] The molecular density was estimated by X-ray reflectometry.(Philips X'PertMRD). Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C/min for thermogravimetry (TG) and a Seiko EXSTAR 6000 DSC 6200 at a heating rate of 10 °C/min for differential scanning calorimetry (DSC) under nitrogen.

Results and Discussion

To obtain a low k polymer, the molecular polarization and/or molecular density of polymers should be minimized. The characteristic feature of our methodology to development of organic low k materials is that monomer **1** has a bulky binaphthyl unit and the polymerization of **1** yields another binaphthyl units in the main chain, which consists of orthogonally bound naphthalene rings. Thus, a novel monomer **1** with a bulky structure was selected as a monomer. The total synthesis of **1** was accomplished from 1,1′-bi-2-naphthol and 1-bromonaphthalene using the Ullmann reaction (Scheme 1).

The structure of monomer **1** was characterized by ^{1}H and ^{13}C NMR and IR spectroscopy and elemental analysis. In the ^{1}H NMR spectrum, a characteristic signal assignable to aromatic protons (a) adjacent to oxygen atom was observed at 6.78 ppm as shown in Figure 1. In the ^{13}C NMR spectrum, signals assignable to ortho (a and k) and para (c) positions of a naphthoxy moiety were observed at 113.4, 125.0, and 123.0 ppm, respectively (Figure 2).

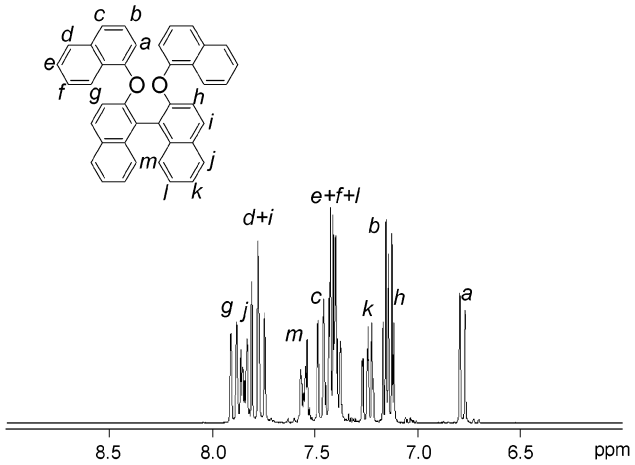


Figure 1. ^{1}H NMR spectrum of monomer **1**.

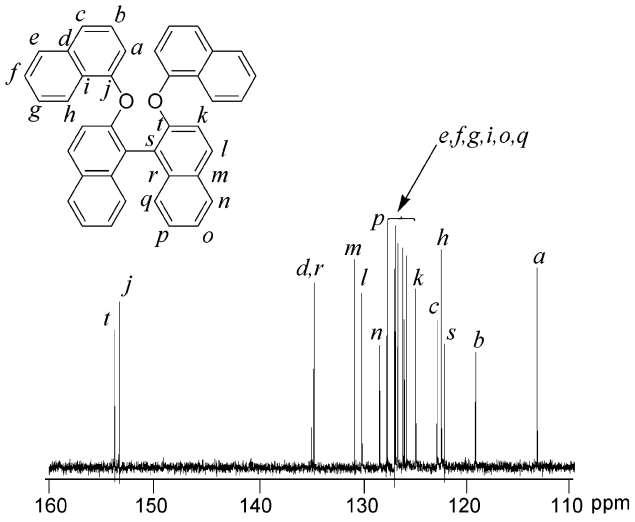
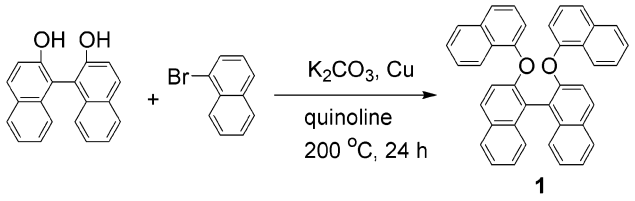


Figure 2. ^{13}C NMR spectrum of monomer **1**.

Scheme 1. Monomer Synthesis



Oxidative coupling polymerization of **1** was carried out by using $FeCl_3$ (2.5−5.0 equiv to **1**) as an oxidant at room temperature for 24 h under a nitrogen atmosphere (Scheme 2 and Table 1). After the polymerization, the resulting polymer was purified by repeated precipitation with methanol containing a small amount of concentrated HCl, followed by washing with ion-exchange resin (Amberlite EG-4HG; organo chem) to remove the iron ions. All the polymers were quantitatively obtained and soluble in chloroform, anisole, cyclohexanone, and nitrobenzene. Decreasing the amounts of $FeCl_3$ from 5.0 to 2.5 equiv increased the M_n values to 11 300. The higher M_n polymer of 13 500 was obtained for the prolonged polymerization time of 48 h.

Scheme 2. Oxidative Coupling Polymerization of 1

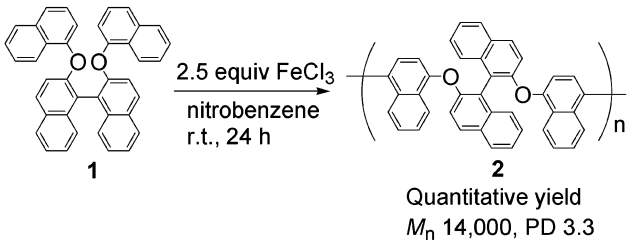


Table 1. Preparation of Polymer 2

run	amount of $FeCl_3$ (equiv)	time (h)	M_n[b]	M_w/M_n[b]
1	5	24	4800	4.2
2	3	24	9300	3.2
3	2.5	24	11300	2.5
4	2.5	48	13500	3.3

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

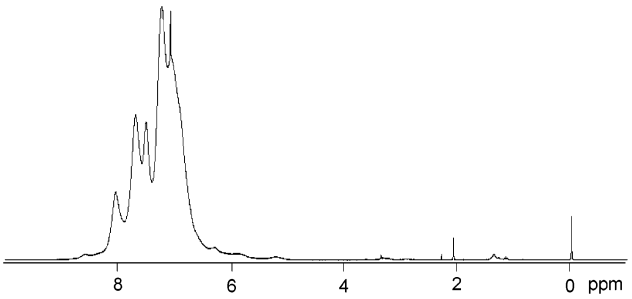


Figure 3. ^{1}H NMR spectrum of polymer **2**.

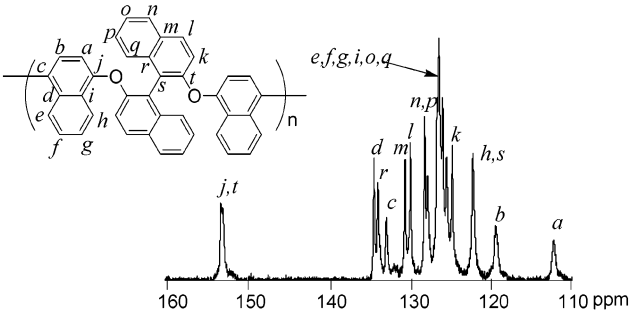


Figure 4. ^{13}C NMR spectrum of polymer **2**.

The structure of polymer **2** was characterized by IR, ^{1}H, and ^{13}C NMR spectroscopy and elemental analysis. The ^{1}H NMR spectrum of polymer **2** shows broad signals mainly due to the restricted conformations from the large repulsion between bulky naphthalene rings (Figure 3). Figure 4 depicts the ^{13}C NMR spectrum of polymer **2**, in which signals assignable to *ortho* (a and k) positions of naphthoxy moiety were observed at 112.7 and 125.3 ppm, respectively. Noticeably, signals assignable to the para position (c) of the naphthoxy group in compound **1** disappeared, and a new signal was observed at 133 ppm. Furthermore, this signal completely disappeared in the ^{13}C-DEPT45 NMR spectrum (Figure 5). These findings clearly indicated that the oxidative coupling reaction selectively occurred at position c, resulting a linear polymer with good solubility.

The physical properties of polymer **2** are summarized in Table 2. The refractive index (n) was measured at the wavelength of 1.32 μm using a prism coupler. The

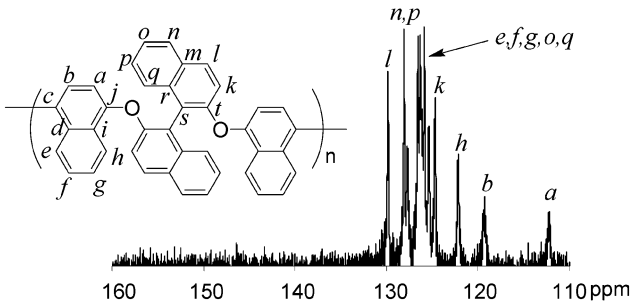


Figure 5. ^{13}C/DEPT45 NMR spectrum of polymer **2**.

Table 2. Properties of 2 and SiLK

properties	**2**	SiLK[f]
ϵ[a]	2.50	2.65
ρ[b] (g/cm^3)	1.13	1.17
n[c]	1.61	1.63
T_d[d] (°C)	470	450
T_g[d] (°C)	301	490
Young's modulus[e] (GPa)	9.8	3.5
hardness[e] (GPa)	0.42	0.38

[a] Dielectric constant at 1 MHz measured from the capacitance. [b] Molecular density estimated by X-ray reflectometry. [c] Refractive index measured by a prism coupler at a wavelength of 633 nm. [d] Measured by TGA and DSC at a heating rate of 10 and 5 °C/min, respectively. T_d indicates the 0.7% weight loss temperature. [e] Determined by the nanoindentation technique. [f] Quoted from ref 4.

Scheme 3. Molecular Polarizabilities (α) and Van Der Waals Volumes (V_{vdw})

$$\frac{\varepsilon-1}{\varepsilon+2}=\frac{4\pi}{3}\frac{N_A\alpha}{M}\rho=\frac{4\pi}{3}\frac{\alpha}{V_{vdw}}K_p$$

in-plane and out-of-plane values of n are 1.614 and 1.608, respectively. Thus, the birefringence is 0.004. The optically estimated ϵ_{op} at 1 MHz was determined to be 2.59, according to the following equation: $\epsilon_{op} = n^2$. To directly measure the dielectric constant of polymer **2**, a polymer film with a thickness of 500 nm was spin-cast onto a silicon wafer from its nitrobenzene solution. The average ϵ value was determined from its capacitance to be 2.50. The molecular density (ρ) of polymer **2** was estimated as 1.13, using X-ray reflectometry.

In an effort to investigate the origin of the low ϵ of polymer **2**, molecular polarizabilities (α) and van der Waals volumes (V_{vdw}) were calculated using the DFT theory for models of aromatic polymers (Scheme 3 and Chart 1). According to the modified Clausius−Mossoti's equation, small values of α/V_{vdw} and/or coefficients of molecular packing (K_p) yield low ϵ, in which the K_p is estimated from V_{vdw}, the molecular weight of the repeating unit (M), the experimental density (ρ) of the polymer, and Avogadro's number (N_A). Naphthalene rings generally increase the polarizability of a molecule, due to increased π-conjugation; therefore, the values of α/V_{vdw} for **1** is comparable to those of imide (**3**) and benzoxazole (**4**) compounds and much higher than that of an aryl ether (**5**). However, the K_p of **A** is significantly lower than those of **B** and **C** and slightly lower than that of **D**. This clearly indicates that the naphthalene rings do not reduce the inherent polarizability of **2**, but the steric repulsion due to the bulky structures in the binaphthyl or diphenylnaphthyl backbones cause weak molecular packing, which leads to the low density and low dielectric constants.

In addition, the thermal properties of polymer **2** were measured as shown in Figure 6. The 5% weight loss

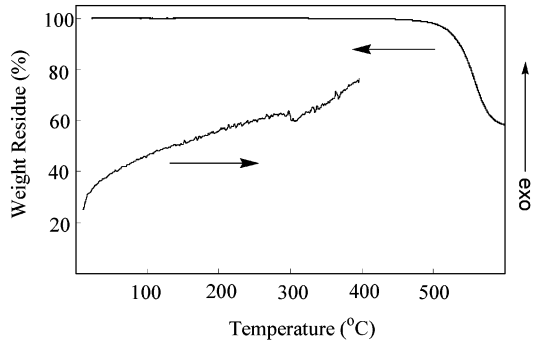
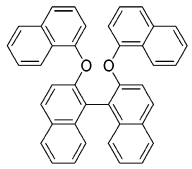


Figure 6. TGA and DSC (second scan) traces of polymer **2** (10 °C/min under nitrogen).

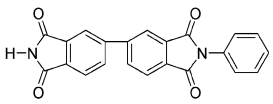
Chart 1. Molecular Polarizabilities (α) of Models Calculated by DFT and Densities (ρ) and Coefficients of Molecular Packing (K_p) of the Corresponding Polymers



A

$\alpha = 73.7\ A^3$, $\alpha/V_{VDW} = 0.147$

[$\rho = 1.13$, $K_p = 0.63$]

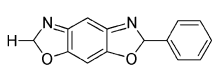


B

$\alpha = 45.3\ A^3$, $\alpha/V_{VDW} = 0.149$

[$\rho = 1.435$~1.475, $K_p = 0.71$~0.73]

The ϵ value of the corresponding polyimide: 3.1

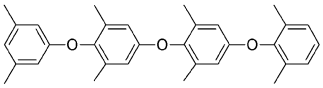


C

$\alpha = 29.4\ A^3$, $\alpha/V_{VDW} = 0.148$

[$\rho = 1.54$~1.56, $K_p = 0.78$~0.79]

The ϵ value of the corresponding polybenzoxazole: 3.0



D

$\alpha = 58.5\ A^3$, $\alpha/V_{VDW} = 0.126$

[$\rho = 1.08$, $K_p = 0.64$]

The ϵ value of the corresponding poly(phenylene ether): 2.5

temperature (T_{5d}) and glass transition temperature (T_g), from thermogaravimetric analysis (TGA) and differential scanning calorimetry (DSC), were 520 and 301 °C, respectively, indicating the high thermal stability of this polymer. The mechanical properties of polymer **2** were measured using nanoindentation techniques. The modulus and hardness of the polymer were determined as 9.8 and 0.42 GPa, respectively, which meet properties required for low *k* materials.

Conclusions

A novel monomer **1** was synthesized from 1,1′-bi-2-naphthol and 1-bromonaphthalene using the Ullmann reaction. The novel poly(binaphthylene ether) **2** was obtained from monomer **1** by oxidative coupling polymerization with the oxidant $FeCl_3$. The number-average molecular weight and polydispersity of polymer **2** were 14 000 Da and 3.3, respectively. The synthesis of monomer **1** and polymer **2** is easy, and a high-temperature curing is also unnecessary. The polymer has a low molecular density and low coefficient of molecular packing, which induces the low dielectric constant of 2.50. This polymer, with its high thermal and mechanical properties as well as its low dielectric constant, will be a good insulating material for future generations of microchips.

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