



# Synthesis and characterization of poly(2,6-dialkoxy-1,5-naphthylene)s with low dielectric constants

Li-Che Hsu<sup>1</sup> · Min Chi Yang<sup>1</sup> · Tomoya Higashihara<sup>2</sup> · Wen-Chang Chen<sup>1</sup> · Mitsuru Ueda<sup>1</sup>

Received: 12 September 2017 / Revised: 3 November 2017 / Accepted: 7 November 2017 / Published online: 15 January 2018  
© The Society of Polymer Science, Japan 2018

## Abstract

An efficient method to decrease dielectric constant ( $\epsilon$ ) of poly(2,6-dihydroxy-1,5-naphthylene) (PDHN) by introducing bulky alkyl side chains was reported. Poly(2,6-dialkoxy-1,5-naphthylene)s (PDANs) were prepared by the *O*-alkylation of PDHN with alkyl halides. The  $\epsilon$  values of PDANs at 10 GHz decreased as the length and size of side chains increased. Especially, PDCHMN exhibited the lowest dielectric constant ( $\epsilon = 2.29$ ). The  $\epsilon$  value results were also supported by refractive index measurement.

## Introduction

Low dielectric constant (low- $k$ ) insulating materials are essential in the electronics industry because they reduce resistance-capacitance time delay, cross-talk, and power dissipation in high-density integrated circuits [1, 2]. Currently, various low- $k$  materials, including fluorinated silica glass, porous silica, and inorganic/organic hybrid materials, have been reported [2]. Additionally, organic polymers, such as poly(imide)s, poly(aryl ether)s, poly(ether ketone)s, hetero-aromatic polymers, and fluoropolymers, have been proposed [1, 2]. Although these polymers exhibit good thermal and mechanical properties, multistep synthesis is required to make these monomers. Thus, a simple procedure for the development of insulating materials remains a challenge. A typical approach to remedy this issue can be found in the synthesis of poly(2,6-dimethyl-1,4-phenylene ether) (PPE) by oxidative coupling polymerization of 2,6-dimethylphenol in the presence of a copper-amine catalyst,

which is atom-economical polymerization [3]. PPE is a typical engineering plastic and has a low dielectric constant ( $\epsilon$ ) of 2.5 [3]. However, its glass transition temperature ( $T_g$ ) is approximately 210 °C, which is inadequate for soldering resistance. In 2003, we reported the convenient synthesis of poly(2,6-dihydroxy-1,5-naphthylene) (PDHN) by Cu(II)-amine-catalyzed oxidative coupling polymerization of 2,6-dihydroxynaphthalene [4]. The polymerization proceeded at room temperature, giving regio-controlled PDHN containing 1,5-linkages. PDHN and its *O*-alkylated polymer, poly(2,6-dibutoxy-1,5-naphthylene) (PDBN) showed relatively low  $\epsilon$  values of 2.82 and 2.75, respectively, as estimated from the refractive index ( $n$ ) of the films according to the modified Maxwell's equation,  $\epsilon = 1.10 n^2$  [5]. In theory, a naphthalene ring is not suitable for improving the  $\epsilon$  value because of its high molar polarization [6]. The low  $\epsilon$  values of PDHN and PDBN may be due to their kinked structures, which arise from orthogonal bonding of naphthalene rings, increasing the free volume of the polymers, thereby decreasing their  $\epsilon$  values [4]. Based on these findings, poly(binaphthylene ether) [7] and poly(naphthylene ether) [8] containing a tetraphenylmethane group were prepared by oxidative coupling polymerization of 2,2'-bis(1-naphthyl-1'-oxy)-1,1'-binaphthyl and 4,4'-bis(1-naphthyl-1'-oxy)tetraphenylmethane, respectively. These polymers exhibited low  $\epsilon$  values of 2.50 and 2.75, respectively. Decreasing the molecular density and molecular polarization according to the Clausius–Mossotti equation is an effective strategy for reducing the  $\epsilon$  value [9, 10]. PDHN has a large number of hydroxyl groups on its backbone. Therefore, modification of the side chains is easily carried out, similar to the

**Electronic supplementary material** The online version of this article (<https://doi.org/10.1038/s41428-017-0011-9>) contains supplementary material, which is available to authorized users.

✉ Mitsuru Ueda  
ueda@ntu.edu.tw

<sup>1</sup> Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

<sup>2</sup> Department of Organic Materials Science, Graduate School of Organic Materials Science, Yamagata University, Yamagata 992-8510, Japan

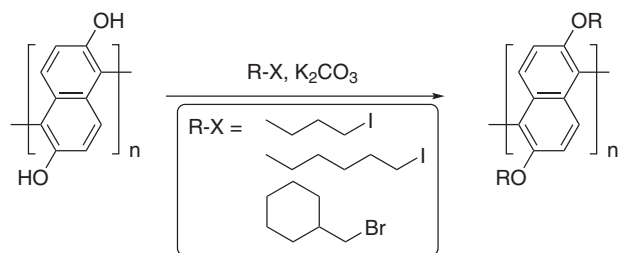
synthesis of PDBN, and introduction of various alkoxy groups in PDHN is expected to improve the  $\epsilon$  values. This paper describes the synthesis and properties of poly(2,6-dialkoxy-1,5-naphthylene)s (PDANs) from PDHN and alkyl halides. The dielectric constants ( $\epsilon$ ) of the PDANs decreased from 2.60 to 2.29 with the increasing length and size of the aliphatic side chains. In particular, poly(2,6-dicyclohexylmethoxy-1,5-naphthylene) (PDCHMN) had the lowest dielectric constant ( $\epsilon = 2.29$ ).

## Results and discussion

### Synthesis of poly(2,6-dialkoxy-1,5-naphthylene)

Oxidative coupling polymerization of PDHN was performed in the same manner as reported in our previous work [4]. PDANs were further synthesized via the aliphatic nucleophilic substitution reaction between PDHN and alkyl halides to reduce their dielectric constants and improve their solubility in organic solvents (Scheme 1).

The results are summarized in Table 1. As seen, PDHN was easily prepared by a 6 h oxidative polymerization at room temperature, as reported in the literature [4]. *O*-alkylation of PDHN with alkyl iodides was carried out at room temperature. PDBN and PDHexN were obtained at moderate yields after 3 d. By contrast, the reaction of PDHN with (bromomethyl)cyclohexane took 5 d even at 60 °C due



Scheme 1 Synthesis of PDANs

Table 1 Preparation of PDHN and PDANs

Polymer	Reaction time	Reaction temperature	Yield (%)	$M_n$ ( $\times 10^{-4}$ ) <sup>a</sup>	PDI <sup>a</sup>
PDHN	6 h	room temp.	80	4.4	1.8
PDBN	3 d	room temp.	61	5.7	2.1
PDHexN	3 d	room temp.	62	3.0	2.6
PDCHMN	5 d	60 °C	47	4.6	4.8

The reaction was carried out with 5 mmol of PDHN and 25 mmol of alkyl halide in 30 mL of dimethylformamide (DMF)

<sup>a</sup>Determined by gel permeation chromatography using polystyrene standards in DMF (PDHN) and tetrahydrofuran (THF) (PDANs)

to the lower reactivity of the alkyl bromide compared to an alkyl iodide.

### Characterization of PDAN

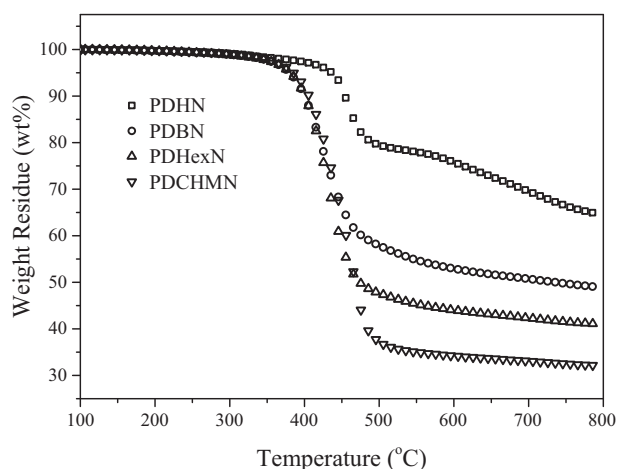
The structures of PDANs were confirmed by Fourier transform infrared (FT-IR), <sup>1</sup>H, and <sup>13</sup>C NMR spectroscopy and elemental analysis. The <sup>1</sup>H NMR spectrum of PDCHMN shows broad signals, mainly due to its restricted conformations because of the large repulsion between bulky naphthalene rings (Figure S1).

The characteristic signal of the hydroxyl groups in PDHN at 8.84 ppm completely disappears, and aromatic signals are observed at 7.24–7.40 ppm (4H). The signal of the methylene protons between the ether and cyclic aliphatic groups appear at 3.81 ppm (4H), and the signals of the cyclic aliphatic group are located at 0.77–1.55 ppm (22H). Furthermore, the <sup>13</sup>C NMR spectrum of PDCHMN with the resonance assignments is shown in Figure S2, where aromatic carbons (*b* and *f*) and characteristic resonances of the methylene carbons (*k* and *r*) adjacent to the ether are observed at 153.8 and 76.0 ppm, respectively.

Figure S3 shows the FT-IR spectra of PDHN and the PDANs. In the IR spectrum of PDHN, a broad, wide band around 3400 cm<sup>-1</sup> was observed due to the hydroxyl groups in the polymer. The characteristic absorption bands of the PDANs were observed at 2958, 2970, 1598, and 1246 cm<sup>-1</sup> due to CH<sub>2</sub> symmetric and asymmetric stretching, C=C stretching and C–O–C stretching, respectively. The structures of the other polymers obtained were determined from the <sup>1</sup>H and <sup>13</sup>C NMR spectra as well as elemental analysis (Fig. S4 and Table S1). The spectroscopic data clearly support the formation of the desired PDANs.

### Thermal properties

The thermal decomposition temperatures of PDHN and PDANs were examined by thermogravimetric analysis (TGA). Figure 1 shows the TGA results for PDHN and PDANs. The 5 and 10 wt% weight loss temperatures ( $T_{d5}$  and  $T_{d10}$ ) of PDHN are 437 °C and 454 °C, respectively, showing the high thermal stability of polynaphthylenes. PDANs also possess good thermal stability over 380 °C. The lower thermal decomposition temperatures of PDANs compared to that of PDHN can be attributed to the introduction of aliphatic side groups. The thermal histories of PDHN and PDANs were tracked by differential scanning calorimetry (DSC) at a heating rate of 10 °C /min and are shown in Figure S5. As seen, no baseline shifts due to the glass transition temperature ( $T_g$ ) were observed up to 300 °C, probably because the rigidity of the naphthalene backbone hinders chain motion when the polymers are heated. These results suggest that PDHN and PDANs are adequate



**Fig. 1** TGA curves of PDHN, PDBN, PHexN, and PDCHMN

**Table 2**  $T_{d5}$ ,  $T_{d10}$ , and  $T_g$  values of PDHN and PDANs

	$T_{d5}$ (°C) <sup>a</sup>	$T_{d10}$ (°C) <sup>a</sup>	$T_g$ (°C) <sup>b</sup>
<b>PDHN</b>	437	454	—
<b>PDBN</b>	380	400	—
<b>PDHexN</b>	381	400	—
<b>PDCHMN</b>	385	406	—

<sup>a</sup>5 and 10% decomposition temperatures as measured by TGA

<sup>b</sup>Glass transition temperature as measured by DSC

for forming insulating materials with excellent thermal stability. Table 2 summarizes the  $T_{d5}$ ,  $T_{d10}$ , and  $T_g$  values of PDHN and PDANs.

### Solubility of PDANs

Table S2 shows the solubility of PDHN and PDANs. PDHN is insoluble in nonpolar organic solvents, such as THF and  $\text{CHCl}_3$ , while PDBN, PDHexN, and PDCHMN are soluble in these solvents. Thus, *O*-alkylation of PDHN is effective at increasing the solubility in nonpolar organic solvents. Transparent films of the PDANs could be cast on a polyimide film from their chloroform solutions (Fig. S6).

### Optical and electrical properties of PDANs

Table 3 summarizes the optical and electrical properties of PDHN and PDANs. Residual copper from the Cu-TMEDA catalyst in polymer samples may affect their electrical properties. Therefore, aluminum oxide column chromatography was performed during the purification steps to eliminate residual copper. As seen in Table 3, the residual copper contents of PDHN and PDANs are all below 20 ppm. The dielectric constants ( $\epsilon$ ) and dissipation factors were measured using a Keysight Network Analyzer

**Table 3** Optical and electrical properties of PDHN and PDANs

	residual Cu <sup>a</sup> (ppm)	$\epsilon$ (10 GHz) <sup>b</sup>	$n^c$	$\epsilon^d$
PDHN	<10 <sup>e</sup>	—	1.65	2.99
PDBN	14	2.61	1.58	2.75
PDHexN	<10	2.60	1.51	2.51
PDCHMN	<10	2.29	1.42	2.22

<sup>a</sup>Residual copper content measured by the Bureau Veritas Company after aluminum oxide column chromatography

<sup>b</sup>Dielectric constant ( $\epsilon$ ) measured at 10 GHz

<sup>c</sup>Refractive index ( $n$ ) at 633 nm measured by ellipsometry

<sup>d</sup>Dielectric constant ( $\epsilon$ ) estimated from the refractive index ( $n$ )

<sup>e</sup>After purification of reprecipitation three times in methanol/water (1/1, vol.) containing HCl without aluminum oxide column chromatography

E5071C at 10 GHz. The dielectric constants of PDANs measured at 10 GHz were below 2.65 and PDCHMN possessed the lowest dielectric constant ( $\epsilon = 2.29$ ) due to having the bulkiest side chains compared to the other PDANs. The small difference in the dielectric constant between PDBN ( $\epsilon = 2.61$ ) and PDHexN ( $\epsilon = 2.60$ ) may be due to side groups connected to the naphthalene backbone in similar configurations.

To confirm the results of the dielectric properties of PDANs, the refractive indices were measured by ellipsometry and the dielectric constants were estimated from the refractive indices according to the modified Maxwell's equation,  $\epsilon = 1.10 n^2$ . The estimated dielectric constants showed a downward trend with the increasing length and size of the side groups connected to the naphthalene backbone, and PDCHMN was estimated to have the lowest dielectric constant ( $\epsilon = 2.22$ ). These results clearly indicate that the introduction of bulky substituents into PDHN decreases the  $\epsilon$  value very effectively.

The  $\epsilon$  value of PDCHMN is very low not only compared to other thermally stable polymers, such as polyarylenes ( $\epsilon = 2.7$ ) [11], poly(arylene ether) ( $\epsilon = 3.0$ ) [12] or aromatic polyimides ( $\epsilon = 3.5$ ) [13], but also compared to the typical low dielectric constant polymer polystyrene ( $\epsilon = 2.5$ ) [14].

### Conclusions

PDANs were successfully prepared via *O*-alkylation of PDHN with alkyl halides. The structures of PDANs were characterized using  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, and FT-IR spectroscopy. PDANs are soluble in THF and chloroform at room temperature and exhibited good thermal stability. Furthermore, no glass transitions were observed in PDANs. The  $\epsilon$  values of PDANs at 10 GHz decreased with the increasing length and size of the side chains. In particular, PDCHMN exhibited the lowest dielectric constant ( $\epsilon = 2.29$ ). These

results indicate that a simple alkylation of PDHN, which is easily obtained from the oxidative coupling of 2,6-hydroxynaphthalene, produces very low- $k$  materials.

## References

1. Maier G. Low dielectric constant polymers for microelectronics. *Prog Polym Sci* 2001;16:3–65.
2. Volksen W, Miller RD, Dubois G. Low dielectric constant materials. *Chem Rev* 2010;110:56–110.
3. Hay AS. Polymerization by oxidative coupling: Discovery and commercialization of PPO<sup>®</sup> and Noryl<sup>®</sup> resins. *J Polym Sci, Part-A, Polym Chem* 1998;36:505–17.
4. Sasada Y, Shibasaki Y, Suzuki M, Ueda M. Convenient synthesis of poly(2,6-dihydroxy-1,5-naphthylene) by Cu(II)-amine catalyzed oxidative coupling polymerization. *Polym (Guildf)* 2003;44:355–60.
5. Boese D, Lee H, Yoon DY, Swalen JD, Rabolt JF. Chain orientation and anisotropies in optical and dielectric properties in thin films of stiff polyimides. *J Polym Sci Part-B Polym Phys* 1992;30:1321–7.
6. Yang C, Jenekhe SA. Group contribution to molar refraction and refractive index of conjugated polymers. *Chem Mater* 1995;7:1276–85.
7. Tsuchiya K, Ishii H, Shibasaki Y, Ando S, Ueda M. Synthesis of a novel poly (binaphthylene ether) with a low dielectric constant. *Macromolecules* 2004;37:4794–7.
8. Tsuchiya K, Ueda M. Synthesis of poly(naphthylene ether) containing tetraphenylmethane group with a low dielectric constant. *Polym J* 2006;38:956–60.
9. Hougham G, Tesoro G, Viehbeck A. Influence of free volume change on the relative permittivity and refractive index in fluoropolyimides. *Macromolecules* 1996;29:3453–6.
10. Seike Y, Okude Y, Iwakura I, Chiba I, Ikeno T, Yamada T. Synthesis of polyphenylene ether derivatives: Estimation of their dielectric constants. *Macromol Chem Phys* 2003;204:1876–81.
11. Goto K, Akiike T, Konno K, Shibata T, Patz M, Takahashi M, Inoue Y, Matsubara M. Thermally stable polyarylenes with low dielectric constant: direction towards the lowest limit of dielectrics. *J Photopolym Sci Technol* 2002;15:223–9.
12. Maier G, Banerjee S, Hecht R, Schneider JM. Poly(aryl ether)s with trifluoromethyl substituents as low- $\epsilon$ -dielectrics for microelectronics. *Polym Prepr (Am Chem, Soc Div Polym Chem)* 1998;39:798–9.
13. Lee YK, Murarka SP, Jeng SP, Auman B. Investigations of the low dielectric constant fluorinated polyimide for use as the interlayer dielectric in ULSI. *Mater Res Soc Sym Proc* 1995;381:31–43.
14. Ahmad Z Chapter 1. Polymeric dielectric materials, Silaghi, M. A. editor., Intech; 2012, pp. 1–26.