Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 47 (2006) 3043–3048

polymer

www.elsevier.com/locate/polymer

Synthesis of novel poly[(1,3-adamantyl)bis(2-naphthol)] with low dielectric constant

Kazuya Matsumoto, Yuji Shibasaki, Shinji Ando, Mitsuru Ueda *

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1-H120 O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Received 8 August 2005; received in revised form 21 February 2006; accepted 22 February 2006

Abstract

A novel thermally stable and low dielectric poly(2-naphthol) containing an adamantyl unit (**3**) has been developed. Polymer **3** was easily prepared by oxidative coupling polymerization of (1,3-adamantyl)bis(2-naphthol) with CuCl(OH)TMEDA as a catalyst. The polymerization produced regiocontrolled polymer **3** with a number-average molecular weight of 10,500 Da and a molecular weight distribution of 4.1. The 5% weight loss temperature of polymer **3** was 480 °C and no glass transition temperature was observed. The dielectric constants (ε) of polymer **3** estimated from the refractive index and the capacitance were 2.92 and 2.96, respectively.

Keywords: Poly(2-naphthol); Low *k* materials; Oxidative coupling polymerization

1. Introduction

Low dielectric constant (low *k*) insulating materials have attracted a great deal of research interest recently owing to substantial improvements of the resistance–capacitance (RC) time delay, cross-talk, and power dissipation in the new generation of high-density integrated circuits [1]. Many insulating materials such as poly(imide)s, poly(aryl ether)s, poly(ether ketone)s, heteroaromatic polymers, and fluoropolymers [2] have been reported. Although, many of these have a very attractive set of properties, relatively high dielectric constant ($\varepsilon > 3$) and a multi-step synthesis has been hindered the application in industries. Cross-linked poly(naphthalene)s (a cured structure is not clear) derived from cyclopentadienone and acetylene-containing materials are very promising materials with the ε of 2.9 and 2.65 estimated from the refractive index ($n = 1.63$) using the equation $\varepsilon = 1.1n^2$ and its capacitance, respectively, and are commercially available under the name of 'SiLK^{R}' [3,4]. Synthesis of monomer and polymer, however, is troublesome and requires high curing temperature (450 °C).

In a preceding paper [5], we reported a convenient synthesis of poly(2,6-dihydroxy-1,5-naphthylene) (PDHN) by Cu(II)-amine catalyzed oxidative coupling polymerization of 2,6-dihydroxynaphthylene. The ε values of PDHN were 2.82 and 2.93 (1 MHz) estimated from the refractive index ($n = 1.60$, $\varepsilon = 1.1n^2$) and the capacitance, respectively, because the large dihedral angle between the neighboring naphthalene rings in its bulky structure causes weak molecular packing, which reduces the density and lowers ε values of the resulting polymer.

In continuation of our research in the preparation of high temperature, high glass transition temperature (T_g), and low *k* materials, a new poly(naphthol) containing an adamantyl unit was designed based on the previous work [6], in which regiocontrolled poly(naphthol) was prepared by oxidative coupling polymerization of bis(2-naphthol). The introduction of an adamantyl group in polymers is expected to decrease the ε value because of its low molar polarization and bulkiness. It is also interesting to compare the effect of the introduction of adamantyl groups and the effect of free volume created by the large dihedral angle between the neighboring naphthalene rings to the ε.

In this paper, we report the synthesis of the new bisnaphthol, (1,3-adamantyl)bis(2-naphthol), its oxidative coupling polymerization with di-μ-hydroxo-bis(N,N,N',N'-tetramethylethylenediamine) copper chloride [CuCl(OH)TMEDA], and characterization of the polymer including thermal properties and dielectric constant estimated from the refractive index.

---

* Corresponding author. Tel./fax: +81 3 5734 2127.
E-mail address: mueda@polymer.titech.ac.jp (M. Ueda).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.02.084

2. Experimental section

2.1. Materials

All reagents and solvents were used as received.

2.2. (1,3-Adamantyl)bis(2-methoxynaphthalne) (**1**)

To the solution of 2-methoxynaphthalene (9.11 g, 57.6 mmol) and 1,3-dibromoadamantane (7.06 g, 24.0 mmol) in chloroform (120 ml) was added $AlCl_3$ (2.13 g, 16.0 mmol). The mixture was heated with stirring for 6 h at 50 °C. The mixture was cooled to room temperature, washed with water, dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated at reduced pressure, yielding the crude product. The product was purified by silica gel column chromatography (toluene/hexane 2/1 in volume ratio). The yield was 6.13 g (57%). Mp 133 °C (by DTA). IR (KBr, ν); 1029 (C–O–C), 1604 (Ph–H), 2900 cm^{-1} ($–CH_2–$). ^1H NMR ($CDCl_3$, δ, ppm): 1.85–2.38 (m, 14H), 3.89 (m, 6H), 7.07–7.14 (m, 4H), 7.47–7.58 (m, 2H), 7.67–7.74 (m, 8H). Anal. ($C_{32}H_{32}O_2$): calcd: C, 85.68%; H, 7.19%; found: C, 85.85%; H, 7.07%.

2.3. (1,3-Adamantyl)bis(2-naphthol) (**2**)

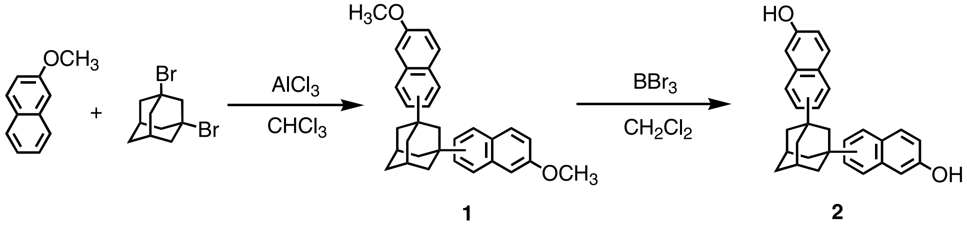
To the cooled solution (−78 °C) of **1** (1.50 g, 3.34 mmol) in dichloromethane (38 ml), a solution of BBr_3 in dichloromethane (6.7 ml, 6.7 mmol) was added under nitrogen. Then the resulting solution was stirred at room temperature for 12 h. The resulting solution was carefully poured into water, extracted using ethyl acetate, dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated at reduced pressure, and the residue was recrystallized from toluene. The yield was 1.03 g (73%). Mp 198 °C (by DTA). IR (KBr, ν); 1604 (Ph–H), 2900 ($–CH_2–$), 3316 cm^{-1} (O–H). ^1H NMR (DMSO-d_6, δ, ppm) (6-position): 1.79 (s, 2H), 1.95–2.04 (m, 8H), 2.11 (s, 2H), 2.29 (s, 2H), 7.06 (d, 1H), 7.09 (s, 1H), 7.52 (d, 1H), 7.61 (d, 1H), 7.69 (s, 1H), 7.71 (d, 1H), 9.31 (s, 1H). ^{13}C NMR (DMSO-d_6, δ, ppm) (6-position): 28.87, 35.19, 36.51, 41.58, 48.34, 108.10, 118.07, 122.10, 123.73, 125.39, 127.58, 128.95, 132.63, 144.29, 154.59. ^1H NMR (DMSO-d_6, δ, ppm) (7-position): 1.79 (s, 2H), 1.95–2.04 (m, 8H), 2.11 (s, 2H), 2.29 (s, 2H), 7.03 (d, 1H), 7.15 (s, 1H), 7.39 (d, 1H), 7.60 (s, 1H), 7.65 (d, 1H), 7.67 (d, 1H), 9.34 (s, 1H). ^{13}C NMR (DMSO-d_6, δ, ppm) (7-position): 28.87, 35.19, 36.51, 41.58, 48.34, 108.80, 117.59, 120.31, 120.67, 125.98, 126.82, 128.17, 134.46, 147.73, 154.94. Anal. ($C_{30}H_{28}O_2$): calcd: C, 85.68%; H, 6.71%; found: C, 85.81%; H, 6.75%.

2.4. Polymerization (**3**)

In a 10-ml round-bottomed flask fitted with a calcium chloride drying tube were placed **2** (0.30 g, 0.713 mmol), CuCl(OH)TMEDA (0.0166 g, 0.0357 mmol), 2-methoxyethanol (1.5 ml), and NMP (1.5 ml). The solution was stirred at 25 °C for 18 h, and poured into methanol containing a small amount of concentrated HCl. A precipitate was dissolved in cyclohexanone, filtered, and reprecipitated with ethyl acetate. The precipitate was collected and dried at 150 °C for 10 h under the reduced pressure. The yield was 0.247 g (83%). IR (KBr, ν); 1596 (Ph–H), 2898 ($–CH_2–$), 3448 cm^{-1} (O–H). ^{13}C NMR (DMSO-d_6, δ, ppm): 28.73, 35.01, 36.24, 41.53, 48.13, 114.69, 117.91, 122.26, 123.02, 123.88, 127.93, 128.18, 132.13, 143.83, 151.98. Anal. ($C_{30}H_{26}O_2 \cdot 0.5H_2O$): calcd: C, 84.28%; H, 6.37%; found: C, 84.15%; H, 6.08%.

2.5. Measurements

Infrared spectra were recorded on a Horiba FT-720 spectrophotometer. ^1H and ^{13}C NMR spectra were obtained on a JEOL JNM-AL400 spectrometer at ^1H, 400 MHz and ^{13}C, 100 MHz. Deuterated dimethyl sulfoxide was used as a 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 Hitachi LC-7000 system equipped with a polystyrene gel column (TSKgel GMH_{HR}-M) eluted with tetrahydrofuran (THF) at a flow rate of 1.0 mL min^{-1} calibrated by standard polystyrene samples. The cyclic voltammogram was measured at room temperature in a typical three electrode with a working (Pt wire), a reference (Ag/AgCl), and a counter electrode (Pt spiral) under a nitrogen atmosphere at a sweeping rate of 10 mV/s (Hokuto Denko HSV-100). A 0.1 M solution of tetrabutylammonium perchlorate in anhydrous acetonitrile was used as an electrolyte. 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), differential thermal analysis (DTA), and a Seiko EXSTAR 6000 DSC 6200 at a heating rate of 10 °C/min for differential scanning calorimetry (DSC) under nitrogen. The film was spin-coated on a silicone wafer from the polymer solution in cyclohexanone. The electrical properties were determined after vapor deposition of chromium with 6×10^{-2} cm^2 square on the surface of the film by using a precision LCR meter (Agilent 4284A 1 MHz). This allowed measuring the capacitance and the breakdown voltage of the films. The dielectric constant ε can be calculated from the capacitance using the formula $\varepsilon = cd/S\varepsilon_0$, where c is the observed capacity, d the film thickness, S the chromium area, and ε_0 the free permittivity. Refractive indices of polymer films formed on quartz substrates were measured at a wavelength of 1320 nm at room temperature with a Metricon model PC-2000 prism coupler. Using linearly-polarized laser light with parallel (TE, transverse electric) and perpendicular (TM, transverse magnetic) polarization to the film plane, the in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices and the film thickness of the samples were determined. The film was spin-coated on a silicone wafer from the solution of polymer in cyclohexanone.



Scheme 1. Synthesis of monomer **2**.

3. Results and discussion

3.1. Synthesis of (1,3-adamantyl)bis(2-naphthol) (**2**)

Monomer **2** was prepared by the Friedel Crafts reaction of 2-methoxynaphthalene and 1,3-dibromoadamantane in the presence of $AlCl_3$, followed by demethylation using BBr_3 (Scheme 1).

The structure of **2** was assigned on the basis of elemental analysis as well as IR and NMR spectroscopy. The IR spectrum of **2** showed characteristic absorptions at 3316 and 2900 cm^{-1} due to the O–H and C–H stretchings, respectively. Fig. 1 shows the ^{1}H NMR spectrum of **2**, consisting of multiplets at 1.79–2.29 (14H) for adamantyl protons, many multiplets at 7.03–7.71 (12H) for naphthalene ring protons, and at 9.31 and 9.34 for naphthol protons (Fig. 1). A full assignment of the aromatic protons was required to determine the coupling position between naphthyl units. Fig. 2 shows the C–H COSY spectrum for aromatic region of **2** with peak assignments. Aromatic protons at *a* and *f* appear at the most upfield (7.06 ppm) and at the second upfield (7.09 ppm), respectively, which are connected with the ^{13}C signals at the 2 (118.07 ppm) and 10 (108.10 ppm) positions, respectively. In contrast, the aromatic protons at *b* and *c* are observed at the most downfield (7.71 ppm) and at the second downfield (7.69 ppm), respectively, and these peaks are connected with the ^{13}C signals at the 3 (128.95 ppm) and 5 (122.10 ppm) positions, respectively. Other signals observed at 7.52 and 7.61 ppm are assigned to the aromatic protons on positions *d* and *e*, respectively. These peaks are correlated with the ^{13}C signals at the 7 (123.73 ppm) and 8 (125.39 ppm) positions, respectively. Other small signals appeared in the ^{1}H and ^{13}C NMR spectra are derived from isomers of **2**, and good correlation between the ^{1}H and ^{13}C signals are observed. From these spectral evidence, monomer **2** is a mixture of three isomers 6,6′-(1,3-adamantyl)bis(2-naphthol), 6,7′-(1,3-adamantyl)bis(2-naphthol), and 7,7′-(1,3-adamantyl)bis(2-naphthol). The ratio of isomers coupled at 6 and 7 positions is 88:12 by using the integrated ratios of the naphthalene ring proton signals at 7.52 (6-position) and 7.39 (7-position) ppm.

It is important to measure the oxidation–reduction potentials of **2** for the selection of oxidants. The cyclic voltammogram of **2** was measured in acetonitrile solution containing 0.1 M tetrabutylammonium perchlorate in a glass cell equipped with a reference electrode (Ag/AgCl), a working electrode (Pt), and an auxiliary electrode (Pt) (Fig. 3). The cyclic voltammogram shows a clear oxidation peak at 0.31 V. Thus, CuCl(OH)TMEDA with the oxidation potential of 0.56 V [6] was selected as the oxidant for oxidative coupling polymerization of **2**.

3.2. Polymer synthesis

Oxidative coupling polymerization of **2** was carried out in the presence of CuCl(OH)TMEDA (5 mol%) at room temperature in air (Scheme 2 and Table 1). 2-Methoxyethanol, 1-methyl-2-pyrrolidinone (NMP) and nitrobenzene that dissolve monomer **2** were used as the polymerization solvents (Scheme 2). The results are summarized in Table 1. Polymerization in 2-methoxyethanol proceeded rapidly in a homogeneous state at the initial stage and then heterogeneously to

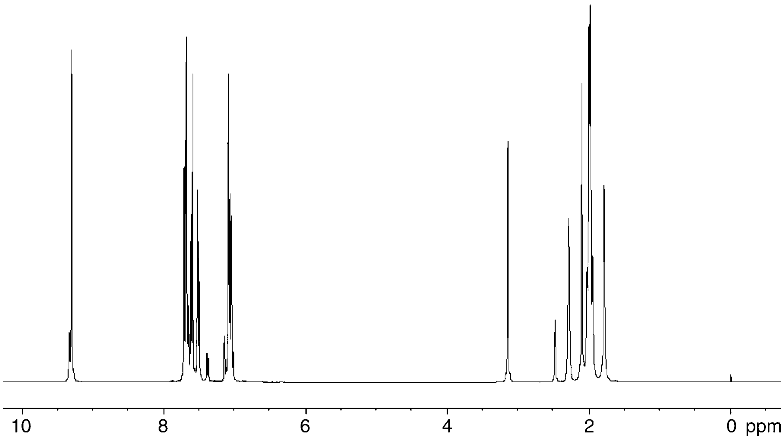


Fig. 1. ^{1}H NMR spectrum of **2** in DMSO-d_6.

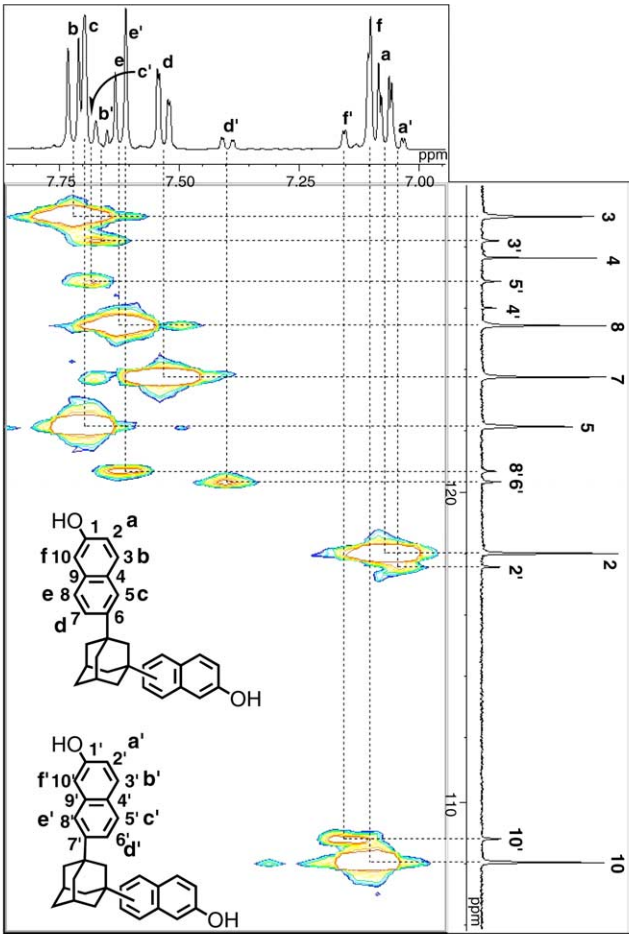


Fig. 2. C–H COSY spectrum for aromatic region of **2** in DMSO-d_6.

give poly(2-naphthol) **3**. On the other hand, polymerization in 1-methyl-2-pyrrolidinone (NMP) and nitrobenzene proceeded homogeneously but slowly. Thus, the mixed solvent, 2-methoxyethanol and NMP, was used, and the high molecular weight polymer was obtained.

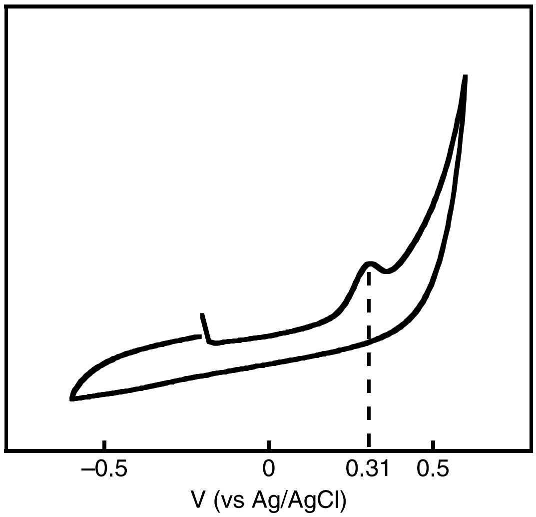
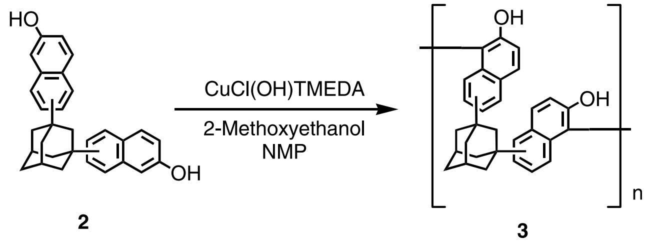


Fig. 3. Cyclic voltammogram of **2** added TMEDA in 0.1 M n-Bu_4NClO_4 solution in acetonitrile, measured at a sweep rate of 10 mV/s.



Scheme 2. Oxidative coupling polymerization of monomer **2**.

3.3. Polymer characterization

The characterization of polymer **3** was performed by IR and NMR spectroscopy and elemental analysis. The IR spectrum of **3** exhibits characteristic absorption at 2898 and 3448 cm^{-1} due to the C–H and O–H stretching, respectively. The ^1H NMR spectrum of **3** shows broad signals mainly due to the restricted conformations by the large repulsion between bulky naphthalene rings. Spectral evidence of the proposed structure of **3** is provided with ^{13}C NMR and DEPT45 spectroscopy. Aromatic regions of ^{13}C NMR and DEPT45 spectra and the assignment of **3** are depicted in Fig. 4. There are 10 intense resonances due to aromatic carbons. The DEPT45 spectrum shows that the signals at 114.69, 127.93, 132.13, 143.83, and 151.98 ppm are the quaternary carbons. The position-10 resonance of 108.10 ppm in **2** shifts to 114.69 ppm in **3**, and then this new signal disappears in the DEPT45 spectrum of **3**. These findings clearly indicate the coupling took place selectively at the 10 position of naphthyl rings, giving regiocontrolled **3**. Elemental analysis also supported the formation of the expected polymer.

Polymer **3** is a yellow solid, soluble in cyclohexanone, THF, nitrobenzene, and dipolar aprotic solvents at room temperature. A transparent film was cast from a solution of the polymer in cyclohexanone.

3.4. Thermal properties

The thermal properties of **3** were examined by TG and DSC. A typical TG trace of **3** is shown in Fig. 5. The polymer shows an excellent thermal stability, and a 5% weight loss temperature (T_{5d}) was 480 °C under nitrogen. The DSC trace exhibits no endothermic peak and baseline shift due to the melting point and the glass transition, respectively. These

Table 1
Preparation of polymer **3** in various polymerization conditions

Run	Solvent	Time (h)	M_n[a]	M_w/M_n[b]
1	2-Methoxyethanol	24	3500	4.5
2	NMP	24	5220	2.2
3	Nitrobenzene	24	1160	3.7
4	2-Methoxyethanol NMP	18	10,500	4.1
5	2-Methoxyethanol nitrobenzene	18	1520	12

[a] Polymerization was carried out with 0.24 mmol of monomer and 5 mol% of CuCl(OH)TMEDA in 1 ml of solvent at 25 °C in air.

[b] Determined by GPC eluted with THF using polystylene standards.

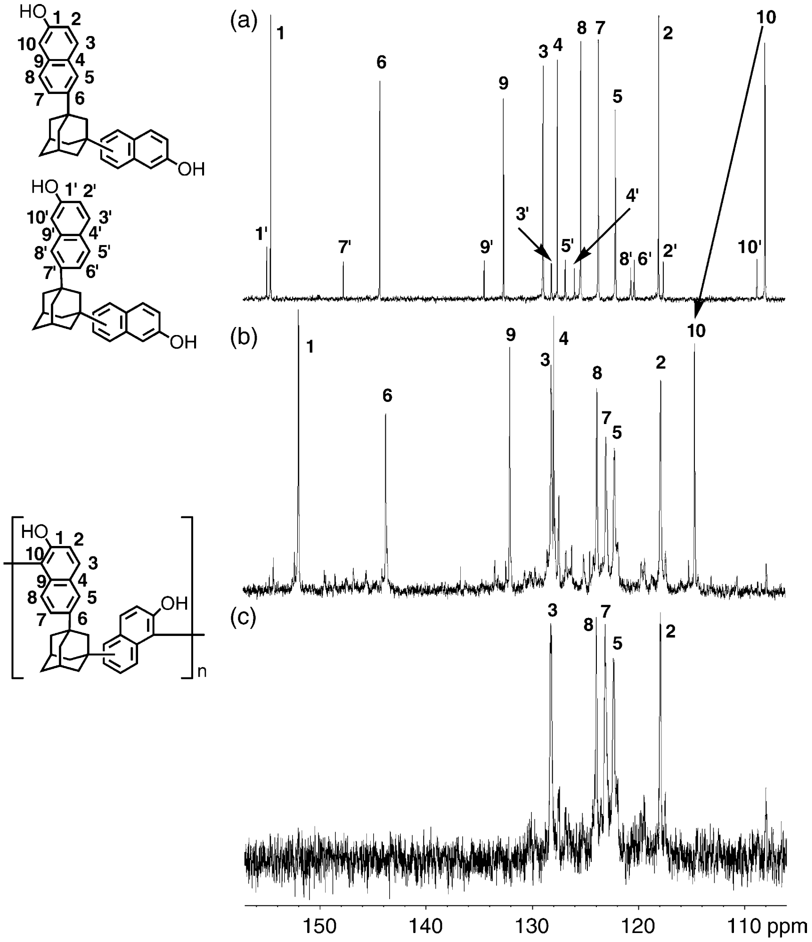


Fig. 4. Aromatic regions of ^{13}C NMR and DEPT45 spectra of **2** and **3**: (a) ^{13}C NMR spectrum of **2**; (b) ^{13}C NMR spectrum of **3**; (c) DEPT45 spectrum of **3** in DMSO-d_6.

thermal properties satisfy the requirement for low *k* materials, because of the rigid structure of **3**.

3.5. Refractive index

The refractive index (*n*) of **3** was measured at the wavelength of 1.32 μm using a prism coupler (Table 2). The in-plane and out-of plane values of *n* are 1.6269 and 1.6369, respectively. Thus, the birefringence is 0.01. The optically estimated ε_{op} at 1 MHz was determined to be 2.92, according to the following equation; $\varepsilon_{op} = 1.1\, n^2$ [7].

In order to measure the *ε* value of **3** directly, the polymer film with a thickness of 1.5 μm was spin-coated onto a silicon wafer from its cyclohexanone solution. The average *ε* value was determined from its capacitance to be 2.96 (1 MHz). Recently, polymers containing triptycene (**4**) was reported to be low *k* materials (ε = 2.78, 10 kHz), because triptycene has restricted rotation by multiple point attachment to the polymer backbones, and introduces free volume at the molecular scale [8]. The *ε* value of **3** is larger than that of polymer **4**, and comparable to that of fluorinated polyimide **5** (*ε* = 2.95, 100 kHz) [9] (Scheme 3). It is interesting that

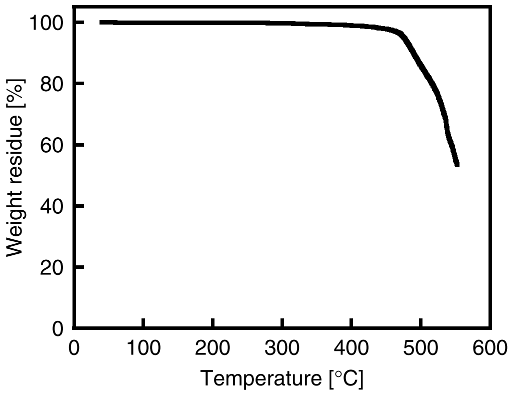


Fig. 5. TG curve of polymer **3** in nitrogen.

Table 2
Refractive indices and dielectric constant of polymer **3**

d (μm)[a]	n_{TE}[b]	n_{TM}[c]	n_{AV}[d]	ε[e]
3.86	1.6269	1.6369	1.6302	2.92

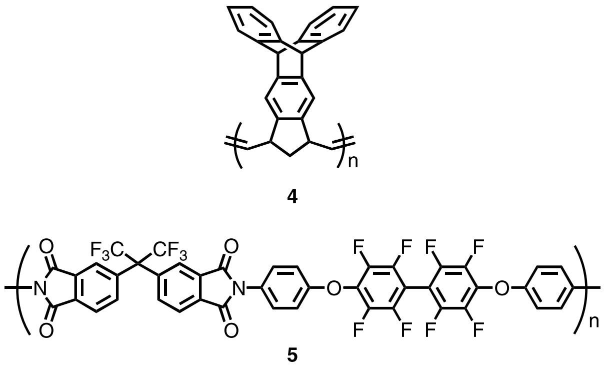
[a] Film thickness.

[b] The in-plane refractive index.

[c] The out-of-plane refractive index.

[d] Average refractive index; $n_{AV} = (2n_{TE} + n_{TM})/3$.

[e] Optically estimated dielectric constant; $\varepsilon = 1.10\, n_{AV}^2$.



Scheme 3. The structure of polymer **4** and **5**.

2,6-dihydroxynaphthylene having a large molar polarization produces low dielectric PDHN. The ε value of **3** is also same to that of PDHN, which means the effect of the free volume created by the large dihedral angle between the neighboring naphthalene rings in PDHN to the ε is almost equal to that of the introduction of adamantyl groups with low molar polarization and bulkiness.

4. Conclusions

Monomer **2** was synthesized from 2-naphthol and 1,3-dibromoadamantane in the presence of $AlCl_3$, followed by demethylation using BBr_3. Polymer **3** was obtained from **2** by oxidative coupling polymerization in the presence of CuCl(OH)TMEDA. The number-average molecular weight and polydispersity of polymer **3** were 10,500 Da and 4.1, respectively. Polymer **3** exhibited a high thermal stability and the relatively low ε of around 3.0. The effect of the introduction of adamantyl group in the main chains of poly(2-naphthol) to the ε is almost same to that of free volume created by the large dihedral angle between the neighboring naphthalene rings in PDHN.

Acknowledgements

The authors would like to express the gratitude to Dr Yoshimasa Sakai (Mitsubishi Chemical Co. Ltd) for the ε measurements.

References

[1] (a) Treichel H. J Electron Mater 2001;30:290.
(b) Havemann RH, Jain MK, List RS, Ralston AR, Shin W-Y, Jin C, et al. Mater Res Soc Symp Proc 1998;511:3.
(c) Morgan M, Ryan ET, Zhao J-H, Hu C, Cho T, Ho PS. Annu Rev Mater Sci 2000;30:645.
(d) The International technology roadmap for semiconductors, San Jose, CA: Semiconductor Industry Association; 2001.
[2] (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.
[3] Shah HV, Brittain ST, Huang Q, Hwu S-J, Whitesides GM, Smith Jr DW. Chem Mater 1999;11:2623.
[4] Martin SJ, Godschalx JP, Mills ME, Shaffer II EO, Townsend PH. Adv Mater 2000;12:1769.
[5] Sasada Y, Shibasaki Y, Suzuki M, Ueda M. Polymer 2003;44:355.
[6] Amou S, Takeuchi K, Asai M, Nizeki K, Okada T, Seino M, et al. J Polym Sci, Part A: Polym Chem 1999;37:3702.
[7] Boese D, Lee H, Yoon DY, Swallen JD, Rabolt JF. J Polym Sci, Part B: Polym Phys 1992;30:1321.
[8] Long TM, Swager TM. J Am Chem Soc 2003;125:14113.
[9] Misra AC, Tesoro G, Hougham G, Pendarkar SM. Polymer 1992;33:1078.