

Synthesis of Poly(naphthylene ether) Containing Tetraphenylmethane Group with a Low Dielectric Constant

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ABSTRACT: A novel thermally stable and low dielectric poly[4,4'-bis(1-naphthoxy)tetraphenylmethane] (2) has been successfully prepared. 4,4'-Bis(1-naphthoxy)tetraphenylmethane (1) as a monomer was synthesized by the Ullmann reaction from 4,4'-dihydroxytetraphenylmethane and 1-bromonaphthalene. The oxidative coupling polymerization of 1 was conducted in 1,1,2,2-tetrachloroethane with iron (III) chloride as an oxidant to afford polymer 2 with number-average molecular weights up to 19,000. The 5% weight loss and glass transition temperatures of 2 were 534 °C and 258 °C, respectively. The dielectric constants (ϵ) of polymer 2 estimated from the refractive index and the capacitance were 2.69 and 2.75, respectively. [doi:10.1295/polymj.PJ2005246]

KEY WORDS Low- κ Material / Poly(naphthylene ether) / Thermal Stability / Oxidative Coupling Polymerization / Insulation Materials /

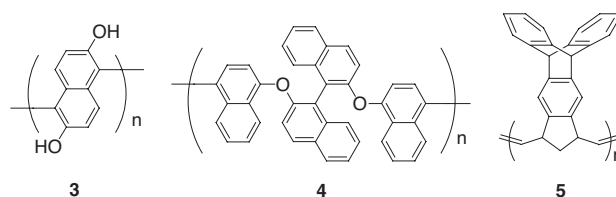
Scaling down of integrated circuit (IC) feature sizes has brought tremendous performance improvement and miniaturization in the past few decades, and the distance of the electrically conducting interconnect lines has extremely decreased.¹ This trend induces resistance-capacitance time delay, crosstalk noise, and power dissipation, which can be improved by the use of either the more conductive metals or low dielectric constant (ϵ) insulators. Many low dielectric constant insulating materials including inorganic, inorganic/organic hybrids, and organic polymers such as poly(imide)s, poly(aryl ether)s, poly(ether ketone)s, heteroaromatic polymers, and fluoropolymers² have been proposed. However, these organic polymers basically comprise high polar aromatic backbone, which results in higher ϵ values except costly perfluoropolymers.³

Recently porous materials have been attracted much attention for low- κ insulators since pores make the density of materials significantly low.⁴ Lower ϵ value can be achieved with pores included inside materials; in the meantime these materials hardly maintain mechanical properties to meet with industrial requirements. Furthermore the high ϵ materials such as an silicon oxide ($\epsilon \sim 3.9$ to 4.5) needs at most 70 percents of pores introduction to reach $\epsilon < 2.0$, which may cause short circuit or metal diffusion through the unisolated pores.

Organic low- κ polymers with much free volume in themselves have also been prepared, mechanical properties of which surpass that of porous materials. Swager *et al.* demonstrated that polymers incorporating the triptycene moiety have pores with a diameter of less than 45 Å by BET gas absorption, which result-

ed in low dielectric constants.⁵ Another example of bulky low- κ polymer is SiLK manufactured by Dow Chemical with high thermal and mechanical properties, but cross-linked system by high thermal treatment is not suitable for industrial process.⁶

On the other hand, we developed a series of poly(naphthylene ether)s 3 and 4 by oxidative coupling polymerization that can produce linear polymers in convenient process,^{7,8} and showed that these polymers have the low dielectric constants of 2.5–2.8, which is maybe explained by molecular size free volume created by their kinked structures due to the orthogonal bonding of naphthalene rings side by side. (Scheme 1) Poly(naphthylene ether)s 3 and 4, however, gave brittle films due to their rigid structure. It is important to prepare polymers giving flexible films as well as decreasing the molecular polarization and molecular density of polymers for the design of low- κ polymers. Introducing a tetraphenylmethane group into polymers will be an effective method to decrease molecular density of polymers because of its bulky tetrahedral structure, which is similar to a 9,9-diphenylfluorene group known as a cardo structure. In addition, incorporation of tetraphenylmethane groups in the main



Scheme 1.

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chains will provide good film properties compared to that of binaphthyl groups that are too rigid to make a film flexible.

This paper describes the successful synthesis of poly[4,4'-bis(1-naphthoxy)tetraphenylmethane] (2) by oxidative coupling polymerization of a novel naphthoxy monomer, 4,4'-bis(1-naphthoxy)tetraphenylmethane (1). The thermal stability and ϵ value of 2 are also reported.

EXPERIMENTAL

Materials

Nitrobenzene was purified by vacuum distillation from calcium hydride. 4,4'-Dihydroxytetraphenylmethane was prepared from dichlorodiphenylmethane and phenol.⁹ Other chemicals were used as received.

Synthesis of 4,4'-Bis(1-naphthoxy)tetraphenylmethane (1)

To a two-necked flask equipped with a dean-stark apparatus were added 4,4'-dihydroxytetraphenylethane (1.4 g, 4.0 mmol), sodium bicarbonate (1.1 g, 8.0 mmol), quinoline (4 mL), and toluene (10 mL), then heated at 150 °C for 2 h to remove water by azeotropy. After the formation of sodium salt, toluene was removed at 150 °C, then the solution was cooled down to room temperature. Copper powder (0.013 g, 5 mol %) and 1-bromonaphthalene (1.2 mL, 8.0 mmol) were added to the solution, followed by heating the mixture at 200 °C for 48 h under nitrogen atmosphere. After the reaction, the mixture was precipitated into the large amount of methanol, and the precipitate was filtrated and washed by methanol. The filtrate was extracted with methylene chloride and 1 N HCl aq. and the organic portion was collected and evaporated. The crude product was purified by silica gel column chromatography eluted with hexane/toluene (1/1) and recrystallized from 1,2-dichloroethane to yield 1.3 g of 1 (54%). ¹H NMR (CDCl₃, 25 °C, ppm): δ = 6.92 (m, 4H), 6.99 (d, 2H), 7.17 (m, 6H), 7.24 (m, 8H), 7.37 (t, 2H), 7.49 (m, 4H), 7.60 (d, 2H), 7.85 (m, 2H), 8.20 (m, 2H). ¹³C NMR (CDCl₃, 25 °C, ppm): δ = 63.97, 113.60, 117.29, 122.11, 123.40, 125.77, 125.89, 125.94, 126.03, 126.59, 126.91, 127.53, 127.78, 131.08, 132.49, 141.57, 146.86, 152.89, 155.87. IR (KBr, cm⁻¹): 1234 (C–O), 1577 and 1596 (C=C, aromatic). Anal. Calcd. for C₄₅H₃₂O₂: C, 89.38%, H, 5.33%. Found: C, 89.49%, H, 5.65%.

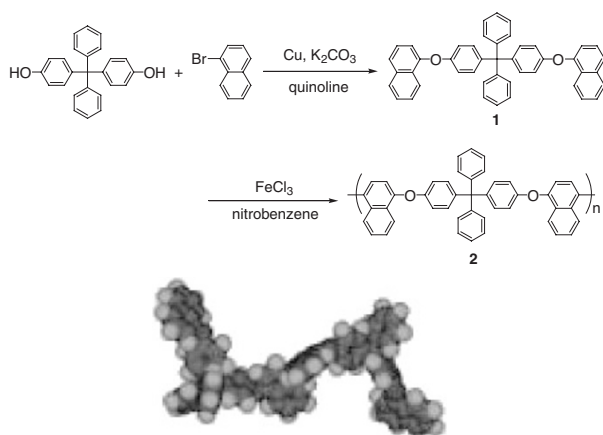
Polymerization of 4,4'-(1-Naphthoxy)tetraphenylmethane

A mixture of 1 (0.10 g, 0.17 mmol) in 1,1,2,2-tetrachloroethane (0.6 mL, 15 wt %) was heated until the solution turned completely clear. After cooling down

to room temperature, iron (III) chloride (0.067 g, 0.42 mmol) was added to the solution under nitrogen atmosphere, and then stirred at room temperature for 48 h. The reaction mixture was poured into methanol, and acidified with a small amount of hydrochloric acid. The polymer was filtrated and dissolved in chloroform, and the solution was precipitated into acetone. White polymer 2 was obtained after filtration. The yield was 0.092 g (92%). ¹H NMR (CDCl₃, 25 °C, ppm): δ = 7.07 (m, 6H), 7.29–7.43 (m, 22H), 8.35 (m, 2H). ¹³C NMR (CDCl₃, 25 °C, ppm): δ = 64.00, 112.80, 117.55, 122.21, 125.83, 126.04, 126.05, 126.64, 126.73, 127.54, 127.89, 131.06, 132.55, 133.49, 134.27, 141.75, 146.81, 152.72, 155.70. IR (KBr, cm⁻¹): 1234 (C–O), 1589 (C=C, aromatic). Anal. Calcd. for C₄₅H₃₀O₂: C, 89.67%, H, 5.02%. Found: C, 89.13%, H, 5.21%.

Measurement

Infrared (IR) spectra were recorded on a Horiba FT-720 spectrophotometer. ¹H and ¹³C NMR spectra were obtained on a JEOL JNM-AL400 spectrometer at 400 and 100 MHz, respectively. Deuterated chloroform 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 Jasco GULLIVER 1500 system equipped with a polystyrene gel column (Pgel 5 μ m MIXED-C) eluted with chloroform at a flow rate of 1.0 mL min⁻¹ calibrated by standard polystyrene samples. 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. The film was spin-coated on a silicone wafer from the polymer solution in toluene. The electrical properties were determined after vapor deposition of chromium with 6×10^{-2} cm² 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 $\epsilon = cd/S\epsilon_0$, where c is the observed capacity, d the film thickness, S the chromium area, and ϵ_0 the free permittivity. Refractive indices (n) 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 deter-



mined. 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 (TBAP) in anhydrous acetonitrile was used as an electrolyte.

RESULTS AND DISCUSSION

Synthesis of Monomer 1

Decreasing the molecular density is an effective strategy for reduction of dielectric constant. Thus novel monomer 1 possessing a bulky backbone was designed and synthesized by the Ullmann reaction from 4,4'-dihydroxytetraphenylmethane and 1-bromonaphthalene using copper catalyst shown in Scheme 2. The structure was confirmed by IR, ^1H NMR, and ^{13}C NMR. The IR spectrum of 1 clearly shows a characteristic absorption at 1234 cm^{-1} due to ether bond (C–O–C) with disappearance of the absorption band due to OH groups. In the ^1H NMR spectrum of 1 (Figure 1a), the signals derived from 1-oxynaphthylene unit appear at 7.37 (b), 7.85 (d), 7.49 (e, f) and 8.20 (g) ppm, especially *ortho*-(a) and *para*-positioned (c) protons appear at 7.60 and 6.99 ppm respectively. Figure 1b shows the ^{13}C NMR spectrum of 1, in which the signals assignable to carbons next to oxygen appear in downfield at 152.89 ppm for *j*-position and 155.87 ppm for *k*-position. In the meantime *ortho*-(a) and *para*-positioned (c) carbons of a 1-oxynaphthylene unit are assigned to 123.40 and 112.80 ppm respectively.

Cyclic Voltammogram

To determine a redox potential of monomer 1, it was measured in a 10 μM acetonitrile solution containing 0.1 M TBAP in the cell equipped with a refer-

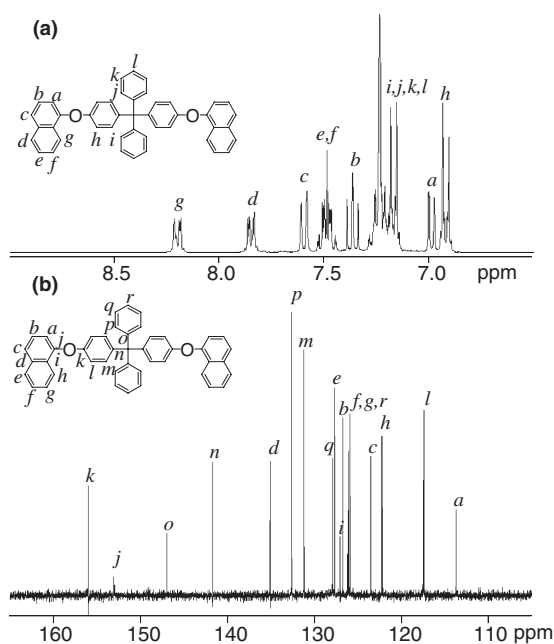


Figure 1. (a) ^1H NMR and (b) ^{13}C NMR spectrum of monomer 1 in CDCl_3 .

Table I. Synthesis of polymer 2^a

Run	Solvent	FeCl_3 (equiv.)	Temp. ($^\circ\text{C}$)	Time (h)	M_n^b	M_w/M_n^b
1	Nitrobenzene	2.2	25	24	3,000	1.9
2	Nitrobenzene	2.5	25	24	4,200	2.4
3	Nitrobenzene	3.0	25	24	4,000	3.4
4	Nitrobenzene	2.5	60	24	1,800	1.8
5	Nitrobenzene	2.5	25	48	4,000	2.0
6	$\text{C}_2\text{H}_2\text{Cl}_4^c$	2.5	25	24	9,600	2.3
7	$\text{C}_2\text{H}_2\text{Cl}_4^c$	2.5	60	24	6,500	2.1
8	$\text{C}_2\text{H}_2\text{Cl}_4^c$	2.5	25	48	19,000	2.3

^aPolymerization was conducted in 15 wt % solution under N_2 atmosphere. ^bDetermined by GPC eluted with chloroform using polystyrene standard. ^c1,1,2,2-tetrachloroethane.

ence (Ag/AgCl), a working (Pt wire), and a counter electrode (Pt spiral). The cyclic voltammogram of 1 reveals that the oxidation potential of 1 is 1.6 V, which is a similar value to that of monomers corresponding to polymer 3 or 4.

Judging from one electron oxidation potential of 1, we selected iron (III) chloride as an oxidant.

Polymer Synthesis

Oxidative coupling polymerization of 1 was carried out in the presence of FeCl_3 under nitrogen atmosphere (Scheme 2). The results are summarized in Table I. Oxidative coupling polymerization requires theoretically 2-equiv of FeCl_3 based on a monomer. The excess amount of FeCl_3 generally increase the rate of polymerization, however, unfavorable gelation may occur due to the extra oxidation of polymers. Therefore, the amount of FeCl_3 is an important factor

for oxidative coupling polymerization. When 2.5 equivalent of iron (III) chloride to monomer 1 in nitrobenzene was used, a number-average molecular weight (M_n) of polymer 2 reached to 4,000. On the other hand, polymerization in 1,1,2,2-tetrachloroethane, which is a better solvent for polymer 2, proceeded smoothly at room temperature, producing quantitatively polymer 2 with the number-average molecular weight (M_n) and polydispersity of 19,000 and 2.3, respectively, after 48 h.

Polymer Characterization

Polymer 2 was white solids and soluble in toluene, chloroform, and tetrahydrofuran (THF). The transparent self-standing film of 2 was prepared from toluene solution. The molecular model of the dimer shown in Scheme 2 illustrates that the highly kinked structure promises to possess high free volumes.

The structure of polymer 2 was identified by IR and NMR spectroscopy. The IR spectrum of 2 showed characteristic absorptions at 1234 and 1589 cm^{-1} due to C–O and C=C stretchings of the naphthyl ether unit, respectively. Elemental analysis also supported the formation of the expected polymer. The microstructure of polymer 2 was investigated by NMR spectroscopy (^1H , ^{13}C , DEPT45). The signal assigned to *c*-positioned proton at 7.60 ppm disappears in the ^1H NMR spectrum of 2, while the signal assigned to *d*-positioned proton at 7.85 ppm shifts to upfield (7.4 ppm) in polymer 2 (Figure 2a). In the ^{13}C NMR spectrum of 2 (Figure 2b), all the signals are observed at similar chemical shifts to monomer assignment except para-positioned carbon (*c*) of the 1-oxynaphthylene unit which significantly shifts from 123.40 ppm for monomer 1 to 133.49 ppm in polymer 2. Moreover, this signal disappears completely in ^{13}C /DEPT45 NMR spectrum shown in Figure 2c, which clearly proves that this carbon changed to the quaternary one. These findings indicate that oxidative coupling reaction selectively occurs at *para*-position of the 1-oxynaphthylene moiety of 1, giving the regio-controlled linear polymer.

Since the relationship between electronic structure and the backbone conformation is an interesting feature of conjugation polymers. Figure 3 shows the UV-vis absorption spectrum of polymer 2 with a peak top at 350 nm. This spectrum is quite similar to that of 1, which indicates a small extension of π -conjugation in polymer 2. This suggests the dihedral angle between neighboring naphthalene rings may be very large because of the steric hindrance of the naphthalene rings. On the other hand, the photoluminescence (PL) spectrum of polymer 2 shows a very smooth peak without any shoulders, indicating no interaction between polymer main chains.

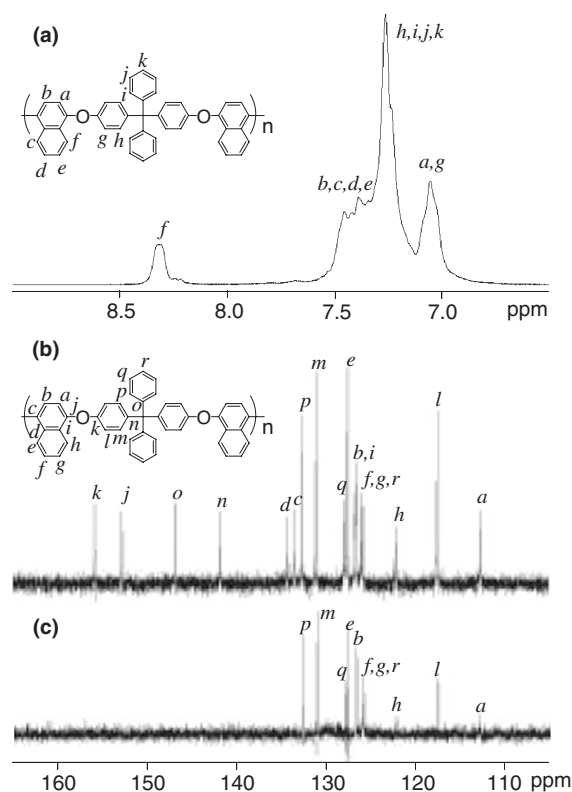


Figure 2. NMR spectra of polymer 2 in CDCl_3 ; (a) ^1H NMR, (b) ^{13}C NMR and (c) ^{13}C /DEPT45 NMR spectrum of 2.

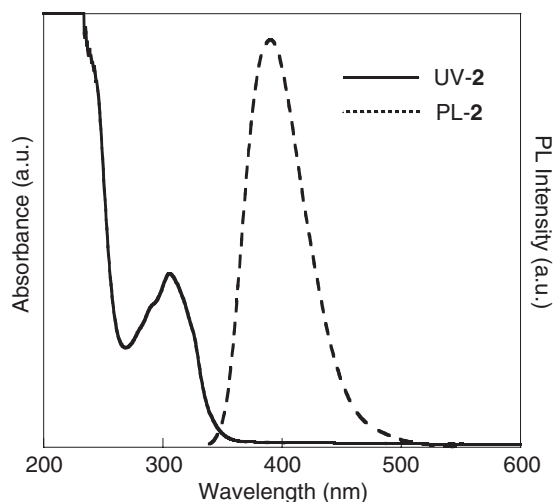


Figure 3. UV-vis absorption (bold line, 1×10^{-7} M) and photoluminescence (broken line, 1×10^{-7} M) of polymer 2 in chloroform solution.

Thermal Stability

The thermal stability of polymer 2 was examined by thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses (Figure 2). In TG profile the polymer showed high decomposition temperature at 534 $^{\circ}\text{C}$ with 5% weight loss. The glass transition temperature (T_g) of 2 was observed at 252 $^{\circ}\text{C}$ in DSC trace on the second heating.

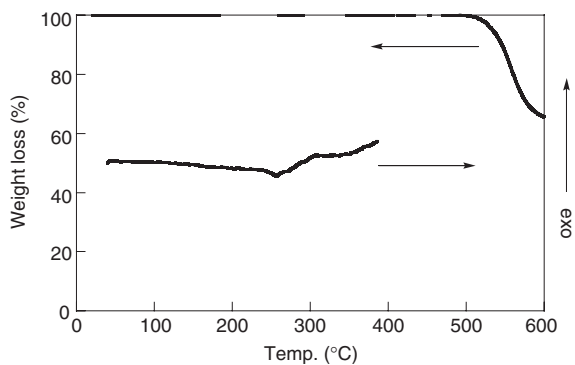


Figure 4. TGA and DSC (2nd scan) traces of polymer 2 (10 °C/min under nitrogen).

Table II. Refractive indices and ϵ values of polymer 2, 3, and 4

Polymer	d (μm) ^a	n_{TE} ^b	n_{TM} ^c	n_{AV} ^d	ϵ_{op} ^e	ϵ^f
2	3.3	1.643	1.638	1.642	2.69	2.75
3	5.0	1.622	1.556	1.600	2.56	2.93
4	5.0	1.614	1.608	1.612	2.60	2.50

^aFilm thickness. ^bThe in-plane refractive indices. ^cThe out-of-plane refractive indices. ^dAverage refractive indices; $n_{\text{AV}} = (2n_{\text{TE}} + n_{\text{TM}})/3$. ^eOptically estimated dielectric constant; $\epsilon = n_{\text{AV}}^2$. ^fDielectric constant calculated from capacitance.

Refractive Index and Dielectric Constant

Finally the physical properties of poly(naphthylene ether)s were summarized in Table II. The refractive index (n) of 2 was measured at the wavelength of 1.32 μm using a prism coupler. The average refractive index value of n is 1.64. The optically estimated ϵ_{op} at 1 MHz is determined to be 2.69, according to the following equation; $\epsilon_{\text{op}} = n^2$,¹⁰ which is similar to that of polymer 3 and 4.

In order to measure the ϵ value of 2 directly, the polymer film with a thickness of 1.3 μm was spin-coated onto a silicon wafer from its toluene solution. The average ϵ value was determined from its capacitance to be 2.75 (1 MHz). Recently, polymers containing triptycene (5) was reported to be low- κ materials ($\epsilon = 2.78$, 10 kHz), because triptycene has restricted rotation by multiple point attachment to the polymer backbones, and introduces free volume at the molecular scale.⁵ The ϵ value of 2 is comparable to that of polymer 5, which means polymer 2 has large free volumes, and, however, is larger than that of polymer 4. These results are summarized in Table II.

The presence of free volume in polymers 2 and 4 was confirmed by BET gas absorption studies that

revealed a surface area for powders polymers 2 and 4 of 124 and 137 m^2/g respectively. Since polymers generally show the surface area less than 20 m^2/g ,¹¹ these results clearly indicate that these polymers involve much free volume.

CONCLUSIONS

A novel monomer 4,4'-bis(1-naphthoxy)tetraphenylmethane 1 was prepared from 4,4'-dihydroxy-tetraphenylmethane and 1-bromonaphthalene by the Ullmann reaction. New naphthylether polymer 2 that has binaphthyl backbone in the main chain was obtained from monomer 1 by oxidative coupling polymerization using iron (III) chloride as an oxidant. The number-average and weight-average molecular weights of polymer 2 were 19,000 and 43,000, respectively. The polymer was capable of making self-standing film by casting from toluene solution, and showed high thermal stability and the low dielectric constant.

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