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Synthesis of thermosetting poly(phenylene ether) containing allyl groups

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Abstract

New thermosetting poly(2-allyl-6-methylphenol-*co*-2,6-dimethylphenol)s (**3**) have been developed by oxidative coupling copolymerization of 2-allyl-6-methylphenol (**1**) with 2,6-dimethylphenol (**2**), followed by thermal curing. Copolymerization was conducted in nitrobenzene in the presence of copper(I) chloride and pyridine as the catalyst under a stream of oxygen, producing high molecular weight copolymers ($M_n \sim 50,000$) with broad molecular weight distributions ($M_w/M_n \sim 35$). The structure of resulting copolymers **3** was characterized by IR, ^{1}H, and ^{13}C NMR spectroscopy. Cross-linking reactions of copolymers were carried out by thermal treatment in the absence or presence of a peroxide (3 wt%, 2,5-dimethyl-2,5-di(*tert*-butylperoxy)-3-butane). The 10% weight loss and glass transition temperatures of the cured copolymers were 436 °C in nitrogen and 235 °C, respectively after curing at 70 °C for 1 h and 300 °C for 1 h. The average refractive index of the cured copolymer (**3b**) film was 1.5407, from which the dielectric constant (ε) at 1 MHz was estimated as 2.6. The ε and dissipation factor of copolymer-films at 1 MHz were directly measured from their capacitances as 2.5–2.6 and 0.0015–0.0019, respectively.

Keywords: Dielectric properties; Low *k* materials; Oxidative coupling polymerization

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1. Introduction

Scaled reduction in interconnect feature size of integrated circuit (IC) has brought a tremendous improvement in the performance in the past few decades, and the distance of the electrically conducting interconnect lines has extremely decreased. Therefore, the insulator separating the conducting elements must have a low dielectric constant in order to minimize the capacitance between lines, and thereby, minimize the “RC” time (R = resistance, C = capacitance), characterizing the delay of signals traveling along lines, and the capacitive “cross talk” between lines [1].

Many low-dielectric-constant polymers have been proposed as insulating materials so far, such as, poly(imide)s, poly(aryl ether)s, poly(ether ketone)s, heteroaromatic polymers, and fluoropolymers [1], however most of them are fluorinated polymers to utilize the low molar polarization of the C–F bond [2]. One of the candidates is a fluorinated poly(aryl ether) which is prepared by nucleophilic displacement of chlorine or fluorine on activated aromatic rings with phenoxides [3]. Non-fluorinated poly(aryl ether)s obtained by the Ullman condensation of aryl dibromides and bisphenols also have been reported [4]. These polymers have a very attractive set of properties, but the syntheses of monomers and polymers require multi-step procedure, resulting in not atom-economical reaction. On the other hand, poly(2,6-dimethyl-1,4-phenylene ether) (PPE), a typical engineering plastic, is prepared by oxidative coupling polymerization of 2,6-dimethyl phenol by copper–amine catalyst, which is an atom economical polymerization [5]. PPE has a low dielectric constant (2.5) and a low dissipation factor (0.0007), however its glass transition temperature is about 210 °C, inadequate for solder resistance. The thermosetting poly(aryl ether) having allyl groups have been developed, in which the polymer shows a low dielectric constant of 2.5, a low dissipation factor of 0.001, and high glass transition temperature of 250 °C, thus is a good candidate as low dielectric and low dissipation materials [6]. However, the synthetic route involving lithiation of PPE followed by allylation with allyl halide is troublesome, and the structure of resulting allylated PPE is not clear due to the possibility of plural allylation in a unit of

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PPE. Therefore, it is interesting to develop a simpler procedure for the development of thermosetting poly(aryl ether)s. The phenol, 2-allyl-6-methylphenol has a crosslinking site after the copolymerization with 2,6-dimethylphenol, and is commercially available.

This article describes the successful synthesis and properties of a new thermosetting poly(aryl ether) containing allyl groups by oxidative coupling copolymerization of 2-allyl-6-methylphenol with 2,6-dimethylphenol, followed by thermal curing.

2. Experimental section

2.1. Materials

2,6-Dimethylphenol (**2**) was purified by recrystallization from *n*-hexane. Pyridine was distilled from potassium hydroxide in nitrogen. 2-Allyl-6-methylphenol (**1**) and copper(I) chloride were purchased from Aldrich and Tokyo Kasei Kogyo Co., Ltd, respectively, and used as received. Other solvents and reagents were used as received.

*2.2. Synthesis of poly(2-allyl-6-methylphenol-co-2,6-dimethylphenol) (**3**) (typical example)*

A two-necked flask equipped with oxygen inlet tube and septum cap was charged with copper(I) chloride (0.021 g, 0.20 mmol), magnesium sulfate (0.20 g, 1.7 mmol), pyridine (1.8 ml), and nitrobenzene (3.3 ml). The mixture was stirred at 20 °C under a stream of oxygen (50 ml/min), yielding a deep-green copper-pyridine complex catalytic solution. To this solution was added a solution of **1** (0.050 ml, 0.33 mmol) and **2** (0.37 g, 3.0 mmol) in nitrobenzene (2.2 ml). The mixture was stirred for 80 min under a stream of oxygen (50 ml/min), and then poured into methanol (300 ml) containing concentrated HCl (5 ml) (MeOH/HCl solution). The precipitate was washed with methanol in several times, dissolved in chloroform, and reprecipitated in MeOH/HCl solution. After washing with methanol and drying at 80 °C for 12 h under vacuum, a white fibrous polymer was obtained. Yield: 0.343 g, 84%. $M_n = 39,000$, $M_w/M_n = 27$.

IR (KBr, ν): 1192 (Ar–O–Ar), 914 and 990 cm^{-1}(C=C). ^{1}H NMR ($CDCl_3$, δ, ppm): 6.47 (s, 2H), 5.85 (m, 0.1H), 4.99 (m, 0.2H), 3.21 (m, 0.2H), and 2.08 (m, 6H). ^{13}C NMR ($CDCl_3$, δ, ppm): 16.76, 113.8, 114.42, 114.74, 116.01, 132.52, 132.78, 134.55, 136.18, 144.88, 145.40, 154.69, 154.89. Anal. $[(C_8H_8O)_9$-*co*-$(C_{10}H_{10}O)_1]$: Calcd. C, 88.82; H, 11.18; Found: C, 88.23; H, 11.41.

2.3. Thermal treatment of the polymer film

The polymer film was prepared by casting from the toluene solution of the polymer on a silicon wafer at room temperature and then heated at 70 °C for 1 h, and 250 °C (or 300 °C) for a specified time under nitrogen.

2.4. Measurements

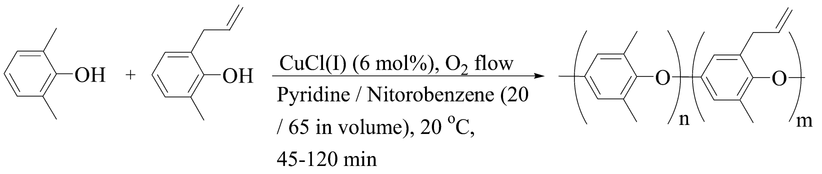
Infrared spectra were recorded on a Horiba FT-720 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded using a BRUKER DPX300 (300 MHz) spectrometer. UV–visible spectra of polymer films were recorded on a Jasco V-560 spectrophotometer. Thermogravimetry (TG), thermo mechanical (TMA), and dynamic mechanical analyses (DMA) were performed with a Seiko TG/DTA 6300, TMA/SS 6100, DMS 6100, heating rate of 3 °C/min under nitrogen, respectively. 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 μm MIXED-C) eluted with chloroform at 40 °C at a flow rate of 1.0 ml/min calibrated by standard polystyrene samples. Refractive indices of polymer films formed on quartz substrates were measured at a wavelength of 1.320 μm 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. Electrical properties at 1 MHz were measured by using impedance analyzer (Yokokawa Electric Co: P4192A) with a dielectric test fixture.

3. Results and discussion

3.1. Polymerization

Although the oxidative coupling polymerizations of **1** were reported to produce the corresponding polymers with low molecular weights [7–9], the copolymerization of **1** with **2** have not been investigated so far. Thus, the synthesis of **3** was carried out by oxidative coupling polymerization of **1** with **2** in the presence of copper(I) chloride and pyridine in nitrobenzene (Scheme 1).

Considering the amount of crosslinking sites in copolymers, the feed monomer molar ratios of **1** and **2** were set in 5/95 (for **3a**) and 10/90 (for **3b**). The copolymerization behavior of 10/90 feed monomer molar ratio is shown in Fig. 1. Copolymerization proceeded smoothly at room temperature, giving high molecular weight copolymers. M_n and M_w of copolymers increased with polymerization time till 80 min, and these values were no longer affected by the time after that. The M_w/M_n values on maturity were ca. 35, which was very broad comparing with that of the commercially available PPE (ca. 8). Generally, excessive broadening of M_w/M_n value is observed when branched polymers are produced by chain transfer reactions to polymer backbones, because such



Scheme 1.

reactions increase as the polymer sizes increase. Thus, branching leads to even more branching as a polymerization proceeds. Branching reactions arise from allyl groups, which are apt to undergo chain transfer.

Based on these results, copolymerizations were performed for 80 min and the results are summarized in Table 1. In both cases, high M_n polymers were obtained in high yields. The compositions of copolymers estimated from the integration ratio between signals at 4.99 (*a*) and 2.1 (*b* and *e*) ppm in ^1H NMR spectrum (Fig. 2) agreed well with the monomer feed ratio, indicating the satisfactory formation of random copolymers.

3.2. Polymer characterization

Copolymers **3** were identified as the expected poly(2-allyl-6-methyphenol-*co*-2,6-dimethylphenol)s by IR, ^1H, and ^{13}C NMR spectroscopies, and elemental analysis. The IR spectra exhibited a characteristic ether absorption at 1192 cm^{-1} (Ar–O–Ar), and a $=CH_2$ out of plane bendings at 990 and 914 cm^{-1}.

The ^1H NMR spectrum of copolymer **3b** exhibited two singlet peaks at 2.08 and 6.47 ppm due to methyl (*b* and *e*) and phenyl protons (*a*, *c*, and *d*), respectively, and the multiplet peaks due to $CH_2{=}CH-$ protons were observed at 4.99 (*h*) and 5.85 (*g*) ppm (Fig. 2). The ^{13}C NMR spectrum of copolymer **3b** is shown in Fig. 3, together with assignment of the observed resonance. No extra peaks were found, clearly indicating the formation of the expected copolymer. However, signals showing branching structures have not been observed, probably because of extremely low contents of branching units.

Copolymers are white fibrous materials, and their films spin-cast from toluene solution are transparent and flexible.

The thermal properties of copolymers **3** were examined by thermogravimetry (TG), thermo mechanical (TMA), and dynamic mechanical analyses (DMA) (Table 2). Because the base line shift due to the glass transition temperature (T_g) of copolymers **3** was not clearly observed in the DSC measurement, T_g values were determined by DMA. Copolymers **3a** and **3b** showed T_g values at 206 and 189 °C, and these increased to 229 and 235 °C, respectively, after curing at 300 °C for 1 h. The coefficient of thermal expansion (CTE) of **3a** and **3b** determined by TMA showed comparable values with that of PPE, indicating that these crosslinking densities in the copolymers were adequate to prevent the large thermal expansion.

3.3. Cross-linking reaction

Cross-linking reactions of copolymers **3** were carried out by thermal treatment in the absence or presence of a peroxide (3 wt%, 2,5-dimethyl-2,5-di(*tert*-butylperoxy)-3-butane) (Fig. 4). The progress of cross-linking reaction for copolymers **3** was followed by the decrease of absorption at 914 cm^{-1} of the vinyl group as shown in Fig. 4. In the absence of the peroxide, thermal treatment at 180 °C produced only 15% consumption of the vinyl groups. On

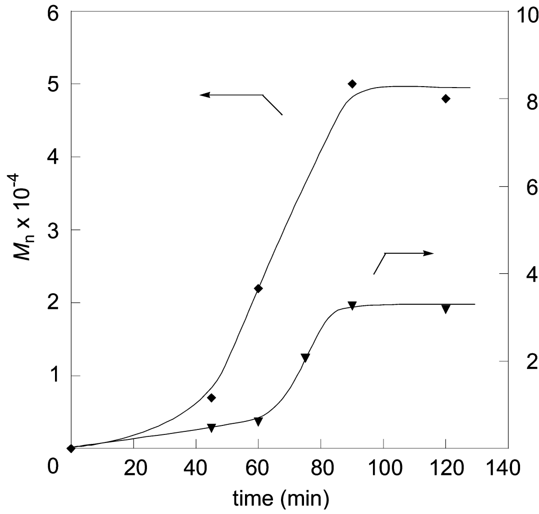


Fig. 1. Copolymerization behavior of **1** with **2** (10:90 molar ratio)

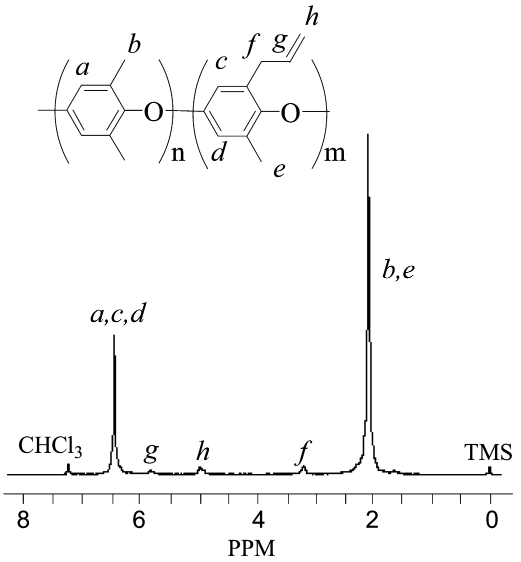


Fig. 2. ^1H NMR spectrum of copolymer **3b** in $CDCl_3$ at 20 °C.

Table 1
Copolymerization of **1** with **2**

Run	[**1**]$_0$/[**2**]$_0$[a]	Yield (%)	Copolymer	M_n[b]	M_w/M_n[b]	Composition[c] in copolymer
1	5/95	83	**3a**	38,000	14	5/95
2	10/90	84	**3b**	39.000	27	10/90

Polymerization was conducted using CuCL (6 mol%) as a catalyst in pyridine/nitrobenzene (20/65 in volume ration) at 20 °C for 80 min under oxygen stream.

[a] Monomer feed ratio.

[b] Determined by GPC (PSt, $CHCl_3$).

[c] Determined by ^1H NMR.

the other hand, the cross-linking reactions easily proceeded by the 1 h curing at 250 °C or at 180 °C with the peroxide resulting in about 60% consumption of the vinyl groups (Fig. 5). High thermal treatment temperature above T_g of copolymers facilitates the movement of main chains and accelerates the cross-linking reactions, and the peroxide is effective to induce the polymerization of the vinyl groups in the allyl groups. Whereas copolymers are soluble in chloroform, dichloromethane, and toluene at room temperature, these cured copolymers are insoluble due to cross-linking.

The cured copolymers **3a** and **3b** (300 °C, 1 h) showed no absorption at 914 cm^{-1} in IR spectra, better thermal stability ($T_{d10} = 433–436$ °C) (Fig. 6), and higher T_g of 229 and 235 °C, respectively, which indicated that the curing promoted crosslinking reaction, resulting in thermally stable resin (Table 2).

As described in Section 1, PPE would be used as insulating materials in semiconductor field. Thus, it is important to measure the dielectric constant (ε) and dissipation factor of copolymers **3b**. The ε at 1 MHz can be estimated from the refractive index n according to modified Maxwell's equation, $\varepsilon = 1.10\, n_{AV}{}^2$ [10]. The film of **3b** on quartz was prepared by spin-cast from toluene solution of **3b**, followed by the successive heating at 70 °C for 1 h, and 300 °C for 1 h under nitrogen. Table 3 summarizes the refractive indices and the calculated dielectric constant of the film. The average refractive index (n_{AV}) of cured copolymer **3b** was determined as 1.5407, which can be translated into the ε of 2.6.

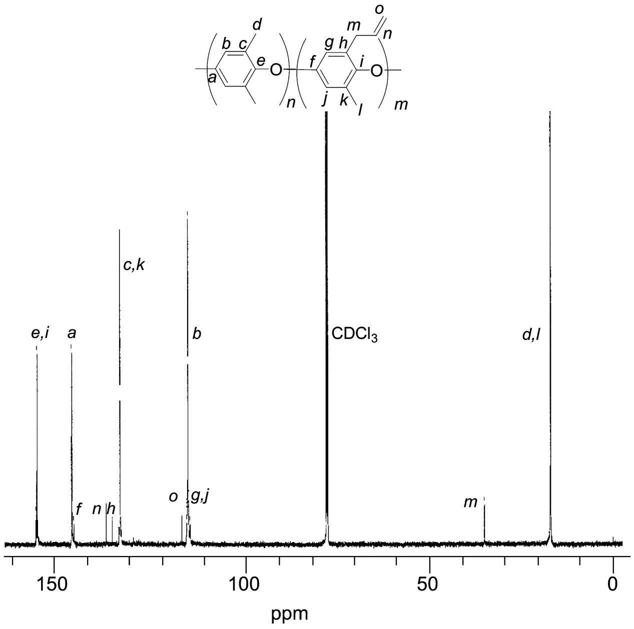


Fig. 3. ^{13}C NMR spectrum of copolymer **3b** in $CDCl_3$ at 20 °C.

Furthermore, the ε and dissipation factor of the cured copolymers **3** were directly measured. The films of copolymers **3** on silicone wafers were prepared by spin-cast from toluene solution of **3**, followed by successive heating at 90 °C for 1 h, and 300 °C for 1 h under nitrogen (film thickness = 3 μm). The wafer was placed in a vacuum chamber and aluminum was deposited. Capacitance measurement was carried out with the aid of an impedance analyzer. Contact was made to the backside of the wafer and via a surface probe to one of the aluminum contacts. The capacitance was measured using a 1 MHz AC signal. The capacitance of ten individual capacitors was measured and the results were averaged. From this capacitance data, the ε was calculated using the following equation:

$$\varepsilon = dC/A\varepsilon_0$$

where d is the thickness of the film, C is the capacitance, A is the area, and ε_0 is the permittivity in a vacuum. The directly measured ε of **3a** and **3b** at 1 MHz were 2.6 and 2.5, respectively. These values are in close agreement with the value calculated from the refractive index, and are comparable to that of PPE ($\epsilon = 2.5$). The dissipation factors of **3a** and **3b** were also determined as 0.0015 and 0.0019, respectively.

Table 2
Thermal properties of **3a**, **3b**, and PPE

Polymer	Cure (°C, h)	T_g[a] °C	T_{d10}[b] (°C)	CTE[c] (ppm/K)
3a	–	206	430	–[d]
3b	–	189	430	–[d]
3b	250,1	221	–[d]	80
3a	300,1	229	433	65
3b	300,1	235	436	66
PPE[e]	–	210	436	65

[a] Glass transition temperature measured by DMA.

[b] 10% weight loss temperature under N_2 determined by TG.

[c] Coefficient of thermal expantion determined by TMA.

[d] Not determined.

[e] Poly(2,6-dimethyl-1,4-phenylene oxide) in Ref. [6].

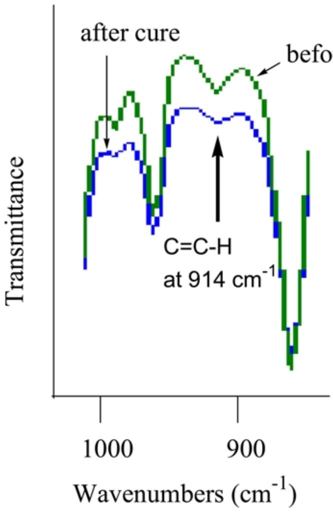


Fig. 4. Progress of cross-linking reaction determined by decrease of the absorption of the vinyl group at 914 cm^{-1}.

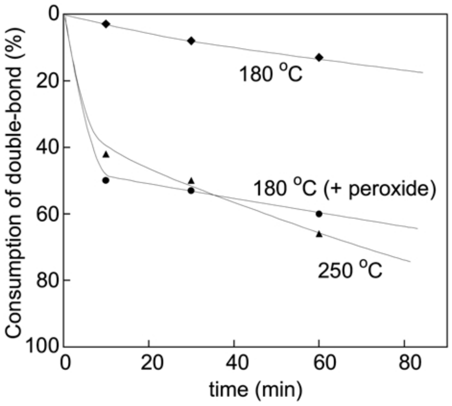


Fig. 5. Relationship between a consumption of double bond in **3** and curing time at 180 °C (diamond), 180 °C with peroxide (triangle), and 250 °C (circle).

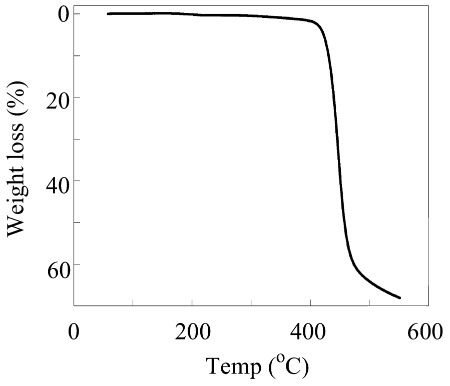


Fig. 6. TG trace for **3b** (cured at 70 °C for 1 h, at 300 °C for 1 h).

Table 3
Refractive index and birefringence of **3b** film

polymer	d (μm)[a]	n_{TE}[b]	n_{TM}[c]	n_{AV}[d]	Δn[e]	ε[f]
3b	5.86	1.5419	1.5385	1.5407	0.0034	2.61

[a] Film thickness.
[b] In-plane refractive index.
[c] Out-of plane refractive index.
[d] Average refractive index; $n_{AV} = (2n_{TE} + n_{TM})/3$.
[e] Birefringence; $\Delta n = n_{TE} - n_{TM}$.
[f] Optically estimated dielectric constant at 1 MHz; $\varepsilon = 1.10\, n_{AV}^2$.

4. Conclusion

New thermosetting poly(2-allyl-6-methyphenol-*co*-2,6-dimethylphenol)s (**3**) were prepared by oxidative coupling copolymerization of 2-allyl-6-methylphenol (**1**) with 2,6-dimethylphenol (**2**) in the presence of copper(I) chloride and pyridine as the catalyst in nitrobenzene under a stream of oxygen. High molecular weights and broad molecular weight distributions of copolymers **3** were produced. Thermally cured copolymers **3** (300 °C, 1 h) showed excellent solvent resistance, high thermal stability, high T_g (229–235 °C), low ε value (2.5–2.6), and the low dissipation factor (0.0015–0.0019). Therefore, these materials would be of useful in high-speed and high frequency printed circuit board application.

Acknowledgements

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