

Low Dielectric Loss Copolymer Obtained from 2,6-Dimethylphenol and 2-Allyl-6-methylphenol via Cu-catalyzed Oxidative Coupling Polymerization

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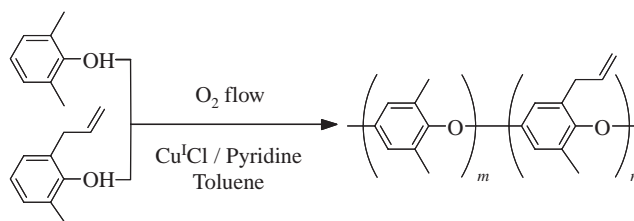
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A method for synthesizing a novel thermosetting poly(2-allyl-6-methylphenol-co-2,6-dimethylphenol) (Allyl-PPE) with a narrow molecular weight distribution (MWD) has been developed. Allyl-PPE was prepared by a pyridine/copper(I) chloride-catalyzed oxidative coupling polymerization of 2-allyl-6-methylphenol (10 mol %) with 2,6-dimethylphenol (90 mol %), using large amounts of pyridine. Allyl-PPE with a narrow MWD showed a lower dielectric constant (ϵ') and dielectric loss tangent ($\tan \delta$) than copolymers with a broad MWD.



Scheme 1. Preparation of Allyl-PPE.

In recent years, the GHz-area has increasingly come to be used for signals from communication equipment such as portable telephones, and the working frequency (f) is expected to become even higher in the future. The dielectric loss (α) of electrical signals is expressed with the dielectric constant (ϵ') and the dielectric loss tangent ($\tan \delta$) by the following eq 1.

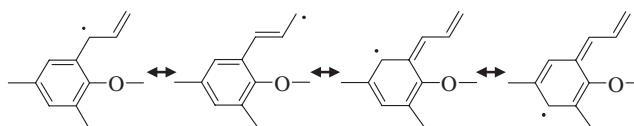
$$\alpha \propto \sqrt{\epsilon'} \cdot \tan \delta \cdot f \quad (1)$$

To avoid large α , it is necessary to develop novel insulating materials with a low ϵ' and $\tan \delta$. Many low-dielectric-constant polymers have been proposed as insulating materials, such as poly(imide)s, poly(aryl ether)s, poly(ether ketone)s, heteroaromatic polymers, and fluoropolymers.¹⁻⁴ Among them, poly(2,6-dimethyl-1,4-phenylene ether) (PPE) is one of the best candidates because of its excellent dielectric properties, ϵ' of 2.5 and $\tan \delta$ of 0.002.⁵ However, its glass transition temperature is around 210 °C, which is inadequate for a lead-free process.

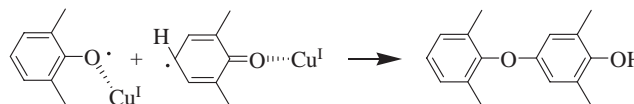
To improve this property, we previously reported the synthesis of thermosetting PPE resins, poly(2-allyl-6-methylphenol (10 mol %)-co-2,6-dimethylphenol (90 mol %)) (Allyl-PPE), with low dielectric properties at 1 MHz by oxidative coupling copolymerization of DMP with AMP (Scheme 1).⁶ These Allyl-PPEs, however, had a broad molecular weight distribution (MWD) (>10), probably due to their branched structures. These branched polymers would vibrate easily on a high frequency of around 10 GHz, so the dielectric loss of the resins rises.⁷ Therefore, it is important to decrease the MWD for insulating materials to be used at high-frequency signals.

This paper reports the successful synthesis of an Allyl-PPE with a low dielectric loss by suppressing the branching even in the presence of the allylic groups by using large amounts of pyridine in a copper(I) chloride.

Allylic hydrogen abstraction from an allyl bond easily occurs, producing an allylic radical in the polymer side chain due to resonance of an allylic radical (Scheme 2). To prevent the formation of a branched structure, the allylic radical formation in the polymer side chains must be suppressed.



Scheme 2. Resonance structures of intermolecular radical unit.



Scheme 3. Terminal reaction of the phenoxy radicals in the coordination sphere of a copper complex.

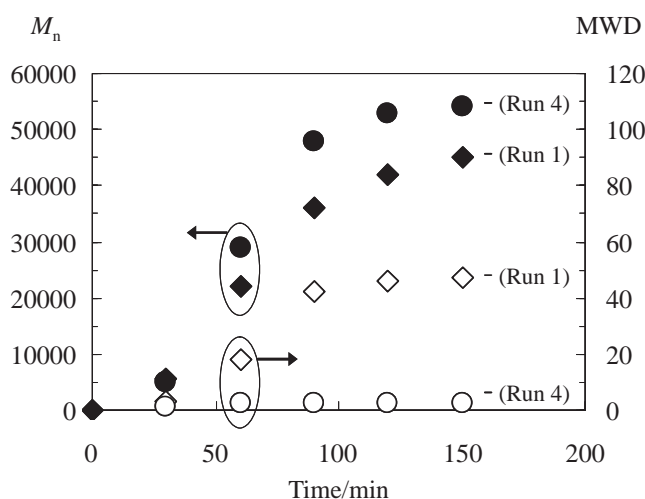
The pyridine ratio in the pyridine/copper(I) chloride catalyst is related to the selectivity of C–O and C–C coupling on the oxidative coupling polymerization of DMP.⁸ The selectivity of C–O and C–C coupling on the oxidative coupling polymerization of 2,6-dimethylphenol increases with increasing the amounts of the complex of copper and pyridine, where the phenoxy radical remains in the coordination sphere of the copper complex. The copper complex increases when a large excess amount of pyridine to Cu was used. Thus, the C–O coupling is promoted, and the C–C coupling, the terminal reaction of polymerization, is suppressed (Scheme 3). On the other hand, coupling of free phenoxy radicals will produce C–C coupling products. The optimum ratio of the pyridine/copper(I) chloride is about 100/1.

From these findings, allylic hydrogen abstraction from the phenoxy radicals remaining in the coordination sphere is expected to be slower than abstraction from free phenoxy radicals. Thus, allylic radical formation will be suppressed, and linear Allyl-PPE will be formed. Therefore, we investigated the effect of the pyridine ratio in the catalyst on oxidative coupling polymerization. The results are summarized in Table 1. The MWD of Allyl-PPE decreased dramatically when the pyridine ratio in the catalyst was increased without changing the M_n . In the

Table 1. Effect of pyridine ratio in a pyridine/copper(I) chloride catalyst in the synthesis of Allyl PPE^a

Run No.	Ligand ratio ^b	M_n	MWD	Yield/%
1	33	36000	42.3	81
2	66	44000	15.6	85
3	330	42000	8.3	88
4	660	47000	2.4	91

^aDMP 3.30 g (27.0 mmol), AMP 0.46 mL (3.0 mmol), Cu^ICl 0.42 g (4.0 mmol), pyridine 10.6 mL (132 mmol, Run 1), 21.2 mL (264 mmol, Run 2), 106.2 mL (1.32 mol, Run 3), 212.4 mL (2.64 mol, Run 4), toluene 150 mL, magnesium sulfate 20.0 g (16.6 mmol), 30 °C, 90 min, under a stream of oxygen (50 mL/min). ^bMole ratio of pyridine and copper(I) chloride (Pyridine/Cu^ICl).

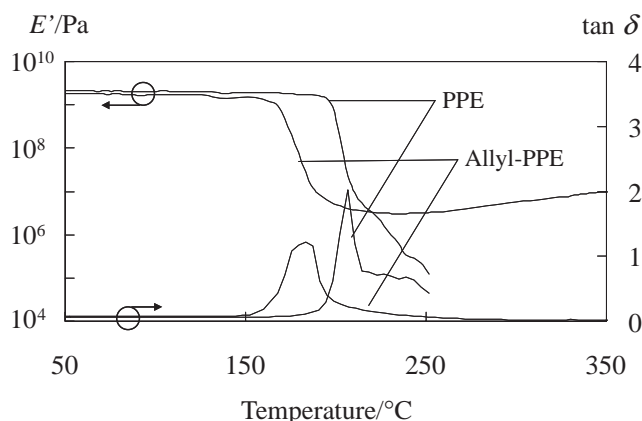
**Figure 1.** Polymerization behavior of Allyl-PPE (for polymerization conditions, refer to Table 1).

presence of 660 times pyridine loading to copper(I) chloride, the MWD of the copolymer reached almost 2. The oxidative coupling polymerization of DMP proceeds in a step-wise manner, so the MWD increases with the extent of reaction and approaches 2 at the limit of large extents of reaction.

The relationship between the M_n of Allyl-PPE and reaction time is shown in Figure 1 for various pyridine/copper(I) chloride ratios. Both the M_n and MWD increased with reaction time in a pyridine/copper(I) chloride ratio of 66 times. In the presence of 660 times excess amounts of pyridine to copper(I) chloride, the M_n increased with the reaction time while retaining a narrow MDW.

Figure 2 shows the stress-strain data of thermal mechanical analysis (TMA/SS) to compare the heat properties of Allyl-PPE to that of PPE with a Seiko TMA/SS 6100. PPE homopolymer softened at around the glass transition temperature (T_g) of PPE. On the other hand, Allyl-PPE maintained a high-storage modulus above T_g . This result indicates that Allyl-PPE is a thermosetting resin, and shows heatproof to molding with the vacuum heating press.

Finally, the ϵ' and $\tan \delta$ of Allyl-PPEs were measured at 10 GHz with an Agilent Technology type 810 network analyzer

**Figure 2.** TMA/SS measurement of Allyl-PPE and PPE (heating rate of 5 °C/min under nitrogen). Molding with the vacuum heating press (1.0 MPa, 260 °C, 1 h), Allyl-PPE: Run 4, PPE: purchased from Aldrich.**Table 2.** Relationship between MWD and the dielectric properties of Allyl-PPE^a

Run No.	M_n	MWD	ϵ' (10 GHz)	$\tan \delta$ (10 GHz)
2	44000	15.6	2.49	0.003
4	47000	2.4	2.41	0.002

^aMolding with the vacuum heating press (1.0 MPa, 260 °C, 1 h).

connecting cavity resonators of Kanto Densi Ouyou. The results are summarized in Table 2. Allyl-PPE (Run 4) with a narrow MWD showed better dielectric properties, because the vibration of Allyl-PPE with fewer branches is suppressed.

In conclusion, we succeeded in preparing thermosetting Allyl-PPEs with a narrow MWD by oxidative coupling polymerization of AMD with DMP using large amounts of pyridine in copper(I) chloride catalyst. The resulting Allyl-PPEs showed excellent dielectric properties due to reducing the amount of branching. These materials would be useful in high-speed and high-frequency printed circuit board applications.

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