

Oxidative Coupling Copolycondensation of 2,6-Dimethylphenol with 2,5-Dimethylphenol: Highly Thermostable Poly(phenylene ether)

By Yuji SHIBASAKI,^{1,*} Kenta HOSHI,¹ Eiichi SUZUKI,¹ Yutaka SHIRAIISHI,² Yasumasa NORISUE,³ and Yoshiyuki OISHI¹

2,5-Dimethylphenol (25DMP) was successfully copolymerized with 2,6-dimethylphenol (26DMP) using the di- μ -hydroxo-bis[(*N,N,N',N'*-tetramethylethylenediamine)copper (II)]chloride (CuCl-TMEDA) catalyst with 10 equiv (to copper ion) of tetramethylethylenediamine (TMEDA) in toluene at 20 °C for 7 h under oxygen. Conversion of the two monomers was monitored by gas chromatography, which revealed that 25DMP was slightly less reactive than 26DMP. Infrared spectra of a series of the copolymers indicated that the composition of the copolymer could be controlled by the monomer feed ratio. The resulting copolymer shows a higher thermal air stability of about 70 °C along with improved mechanical properties in comparison with the conventional poly(2,6-dimethyl-1,4-phenylene ether) (PPE). PPE with a methyl end group, prepared by the endcapping reaction of PPE with methyl iodide in the presence of potassium hydroxide in *N,N*-dimethylformamide, shows a higher thermal stability than the as-prepared PPE under air, and similar stability under nitrogen, indicating that thermal degradation mainly occurs from the polymer end group under air. Thus, the higher thermal stability of the copolymer is attributable to the 25DMP unit located at the end of the copolymer.

KEY WORDS: Oxidative Polymerization / 2,5-Dimethylphenol / 2,6-Dimethylphenol / Copper Catalyst / Degradation /

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) is a widely accepted engineering plastic used in a variety of fields because of its good mechanical, dimensional stabilities, low water uptake, and low dielectric characteristics.¹ However, PPE is likely to decompose under exposure to ultraviolet radiation, resulting in yellowing.² Yellowing is a fatal issue for organic polymer materials. Hindered amines are the typical antioxidant, which trap radical species to form stable nitroxy radical.³ Ultraviolet radiation stable PPE was also prepared by incorporating hindered amines as an additive.⁴ However, it is difficult to improve the ultraviolet radiation stability only by the chemical modification of PPE despite of the reports on highly thermostable crosslinked PPE resin.⁵ Furthermore, due to the low oxidative stability of the polymer, blending with another plastic such as polystyrene is required in order to decrease the glass transition temperature for injection processing.⁶ Thus, currently the potential of PPE remains unfulfilled in terms of application to industry.

Notably, none of the phenol derivatives, with the exception of 2,6-dimethylphenol, are available as conventional oxidative coupling polymerization monomers with a copper-amine catalyst because of radical propagation; thus development of a novel high performance PPE has been strictly limited to date.

Hay *et al.* reported that catalysis using CuCl with a 2-alkyl pyridine such as 2-tridecylpyridine was effective in the synthesis of a high-molecular-weight poly(*o*-cresol);⁷ however,

branching could not be completely excluded. Higashimura *et al.* reported on the use of a tridentate copper catalyst, a μ - η^2 : η^2 -peroxo dicopper (II) complex, in conjunction with a bulky 2,6-diphenylpyridine base for the regio-controlled polymerization of 2,5-dimethylphenol (25DMP), where the resulting polymer, poly(2,5-dimethyl-1,4-phenylene ether) (PPE25), had an average molecular weight (M_n) of 4,000 and a molecular weight distribution (M_w/M_n) of 4.9.⁸ Although this catalytic system could then be applied to the polymerization of other phenol derivatives such as *o*-cresol⁹ *m*-cresol,¹⁰ and *p*-phenoxyphenol,¹¹ perfect regio-regularity has not been realized. A mesoporous supported copper-amine catalyst was prepared and applied to the oxidative polymerization of 2,6-dimethylphenol (26DMP)¹² and 25DMP,¹³ in which a perfectly regio-controlled polymer was obtained. This catalyst was also applied to the regio-controlled oxidative polymerization of *o*-cresol,¹⁴ but the regio-regularity was only about 90%. These results suggest that careful design of the catalytic environment is vital in achieving regio-selectivity in phenol polymerization. A more simple and homogeneous catalytic system based on CuCl with 150 equiv of 2-(*p*-tolyl)pyridine has also been employed for the polymerization, giving excellent regio-regularity of the resulting PPE25; the melting temperature and the degree of crystallinity of the PPE25 were 310 °C and 42%, respectively.¹⁵ Very recently, a di- μ -hydroxo-bis[(*N,N,N',N'*-tetramethylethylenediamine)copper (II)]chloride

¹Department of Chemistry & Bioengineering, Iwate University, 4-3-5 Ueda, Morioka 020-8551, Japan

²Mitsubishi Engineering-Plastics Corporation, 5-6-2, Higashiyawata, Hiratsuka 254-0016, Japan

³Mitsubishi Gas Chemical Co., Inc. Specialty Chemicals Company Planning & Development Division, Mitsubishi Building 5-2, Marunouchi 2-Chome, Chiyoda-ku, Tokyo 100-8324, Japan

*To whom correspondence should be addressed (Tel: +81-19-621-6322, Fax: +81-621-6322, E-mail: yshibasa@iwate-u.ac.jp).

ride (CuCl-TMEDA) catalyst was found to promote the regio-controlled oxidative polymerization of 25DMP with less base additive required (tetramethylethylenediamine 3 equiv to CuCl), although the regio-regularity was not perfect.¹⁶ PPE25 is a semi-crystalline polymer that shows improved thermal and mechanical properties compared with the conventional PPE, but suffers from poor solubility in typical organic solvents; thus, the molecular weight of PPE25 is always about 5,000 or below. We anticipated that copolymerization of 25DMP with 26DMP would provide better thermal and mechanical properties than those of conventional PPE. By such a method, the potential of PPE could be realized without the need for blending with another thermoplastic.

Herein, we report on the oxidative coupling copolymerization of 25DMP with 26DMP with a CuCl-TMEDA catalyst and the properties of the resulting copolymer.

EXPERIMENTAL

Reagents

25DMP and 26DMP were purified by recrystallization with hexane, followed by sublimation, and stored under nitrogen. The CuCl-TMEDA complex was purchased from Tokyo Chemical Industry Co., Ltd. and used as received. All the other reagents and solvents were used as received.

Polymerization

Typical procedure of copolymerization with PPE25_x (*x*: molar ratio of 25DMP): Into a two-necked flask were added 26DMP (9.80 g, 80.2 mmol), 25DMP (0.20 g, 1.63 mmol), and toluene (130 mL). CuCl(OH)TMEDA (0.952 g, 2.05 mmol, 2.5 mol % to the monomer) and TMEDA (4.75 g, 40.9 mmol) were added in this order. The flask was purged with oxygen two times and the mixture was stirred at 20 °C for 7 h. The resulting solution was poured into methanol (1.8 L) containing 20 mL of concentrated aqueous hydrogen chloride to precipitate the polymer. The precipitate was collected, dissolved in toluene (170 mL), and reprecipitated with methanol (1.2 L) containing 10 mL of concentrated aqueous hydrogen chloride. This reprecipitation procedure was repeated two more times to ensure removal of copper ions. The polymer was collected and dried at 100 °C for 12 h under vacuum (PPE25₂ 8.21 g, 85.4% yield).

Kinetic Study

In the next stage and in the following order, 26DMP (1.00 g, 8.26 mmol), 25DMP (1.00 g, 8.26 mmol), octadecane (0.210 g, 0.826 mmol) and toluene (25 mL), CuCl(OH)TMEDA (0.192 g, 0.413 mmol, 2.5 mol % to the monomer) and TMEDA (0.959 g, 8.26 mmol) were added to a two-necked flask. The flask was purged with oxygen two times, and the polymerization solution was fractionated in the set time to measure the consumption of the monomers by GC using octadecane as an internal standard.

End Functionalization of PPE

Into a Erlenmeyer flask PPE (0.122 g, $M_n = 1,300$), KOH

(0.65 g, 11 mmol), toluene (6 mL), and *N,N*-dimethylformamide (6 mL) were added at 0 °C, and the mixture was stirred until the polymer was completely dissolved. Methyl iodide (1.40 g, 10.0 mmol) was then added to the solution, and reacted at 0 °C for 2 h. The reaction solution was transferred to a separating funnel containing water, and the organic compounds were extracted with dichloromethane twice. The organic layer was concentrated by a rotary evaporator, and dropped into methanol to precipitate the polymer. The resulting precipitate was dried at 150 °C for 12 h under reduced pressure (0.048 g, 40% yield, almost 100% functionality). The end functionality was determined by the complete disappearance of the hydroxyl polymer end group at 4.238 ppm in the ¹H NMR spectrum and the corresponding appearance of the methyl ether proton at 3.669 ppm.

Estimation of Polymer Composition

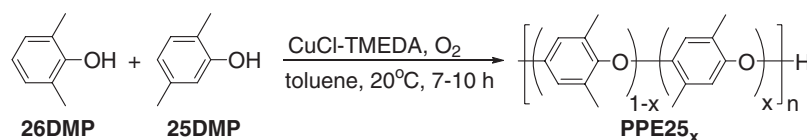
The composition of the copolymers was determined from the intensity ratio of C-H wagging absorption of two segments, 26DMP and 25DMP, in the IR spectrum. Calibration was performed using six polymer samples prepared by blending PPE and PPE25 homopolymers.

Film Preparation

On a press-molding machine, SUS, Teflon (0.1 mm in thickness), Upilex (1 mm in thickness), and an aluminum mold (10 (L) × 110 (W) × 2 (H) mm) were placed in this order. The mold was filled with the well-crushed polymer powder, and the film thickness was adjusted with Teflon rod that was placed upon the sample. Upilex, Teflon, and SUS plates were placed on it, and the sample was pressed at 5 MPa at 220 °C for 10 min, followed by at 280 °C for 20 min at this pressure.

Measurements

Fourier transform infrared (IR) spectra were measured with a Jasco IR-5500 (Jasco Co., Ltd.) by transmittance absorption spectroscopy (KBr tablet method). Number and weight average molecular weights (M_n and M_w) were measured by gel permeation chromatography (GPC) on a Tosoh HLC-8120 GPC equipped with consecutive polystyrene gel columns (TSK-GEL GMH_{HR}-M and GMH_{HR}-N) at 40 °C eluted with chloroform at a flow rate of 1.0 mL min⁻¹ calibrated by standard polystyrene samples. Gas chromatography (GC) was performed on a Shimadzu GC-2010 equipped with a packed silica gel column (Chromosorb W 60/80 AW) at 180 °C with a helium carrier using a hydrogen-flame ionization detector. Octadecane (GC standard grade) was used as an internal reference. Nuclear magnetic resonance (NMR) was performed on a Bruker AC-400P spectrometer at 400 MHz for ¹H and 100 MHz for ¹³C measurement. Deuterated chloroform (CDCl₃) was used as a solvent with tetramethylsilane as an internal reference. Thermal analyses were performed on a Seiko thermal analyzer (SCC 5200 system) at a heating rate of 10 °C/min for thermogravimetric analysis (TGA by TG/DTA 320) and 2 °C/min for dynamic mechanical analysis (DMA by DMS 210) under air or nitrogen. Differential scanning



Scheme 1.

 Table I. Copolymerization of 26DMP with 25DMP^a

Sample	Monomer	Polymer	Feed /mol%	Time /h	Yield /%	Composition ^b 26DMP: 25DMP	M_n^c	M_w/M_n^c
1	25DMP	PPE25	100	8	55	0:100	—	—
2	26DMP+25DMP	PPE25 ₇₀	30:70	8	52	54:44	8,500	3.4
3	26DMP+25DMP	PPE25 ₅₀	50:50	8	56	63:37	7,400	3.1
4	26DMP+25DMP	PPE25 ₃₀	70:30	10	73	62:38	7,400	3.0
5	26DMP+25DMP	PPE25 ₂₀	80:20	7	61	86:14	7,800	2.3
6	26DMP+25DMP	PPE25 ₁₀	90:10	7	71	92:8	7,200	2.2
7	26DMP+25DMP	PPE25 ₅	95:5	7	86	93:7	6,900	2.0
8	26DMP+25DMP	PPE25 ₃	97:3	7	67	94:6	10,000	2.0
9	26DMP+25DMP	PPE25 ₂	98:2	7	86	95:5	10,400	2.0
10	26DMP+25DMP	PPE25 ₁	99:1	7	71	97:3	8,500	2.0
11	26DMP	PPE	100	1.5	67	100:0	10,300	2.2

^aConditions: CuCl(OH)TMEDA 2.5 mol %, TMEDA 10 equiv to copper ion, 20 °C. ^bDetermined by C-H wagging absorption in IR spectrum. ^cDetermined by GPC (CHCl₃, PSt standard).

calorimetry (DSC) was analyzed on Shimadzu DSC-60 at a heating rate of 20 °C/min under nitrogen. The refractive index of the polymer films was measured on an Atago DR-M4 Abbe refractometer. Press-molding of the polymer samples was performed on a Toyoseiki Mini Test Press-10 at 5 MPa pressure and 280 °C for 20 min. The mechanical properties of the polymer films (50 mm × 5 mm) were measured by a Shimadzu AGS-D mechanical analyzer at a pulling rate of 10 mm/min. Measurement of the dielectric constant (ϵ) and dielectric loss ($\tan \delta$) was performed by a cavity resonance method.

RESULTS AND DISCUSSION

Copolymerization

We selected the CuCl-TMEDA catalyst because this catalyst is effective in the regio-controlled oxidative coupling polymerization of both 25DMP and 26DMP (Scheme 1). Table I summarizes the results of the polymerization. As already reported, a regio-regular homopolymer is available from 25DMP in moderate yield as a white powder (sample 1),¹⁶ which precipitates during polymerization. For molding by a press machine, the polymer samples must be effectively crushed into a powder to remove any air voids and to decrease the melt viscosity; a M_n value of around 10,000 is favorable. Thus, various copolymers (PPE25_x, where x indicates the mol% of 25DMP in the feed) with moderate M_n (around 10,000) were prepared by varying the polymerization time. When the feed of 25DMP was increased, the yield of the copolymer increased. The composition of the copolymer was estimated by the wagging absorption of the aromatic C-H bonds apparent at 857 and 885 cm⁻¹ for PPE and PPE25, respectively. The composition of the copolymer was controlled

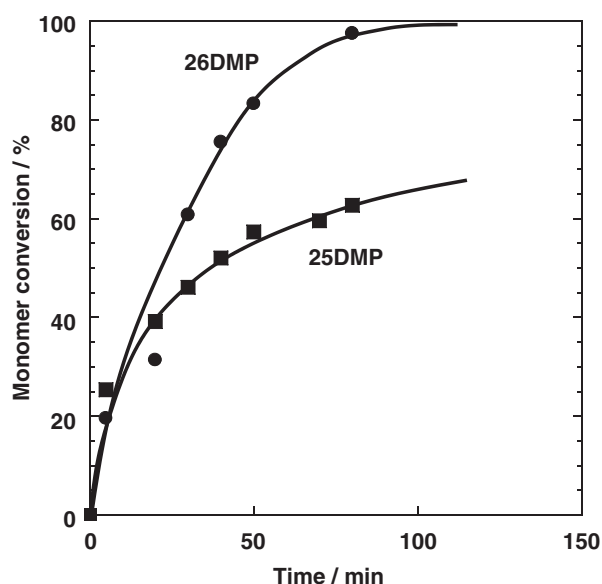


Figure 1. Time-conversion curves of 26DMP and 25DMP in the copolymerization reaction (1:1 in molar ratio).

by the monomer feed ratio, but the ratio of 25DMP in the copolymer gradually decreased in the high feed region (sample 2 and 3).

In order to investigate the copolymerization behavior in detail, the monomer conversions were monitored by GC using octadecane as an internal standard. As shown in Figure 1, both monomers were similarly converted into the polymer chain in periods of time up to 30 min, but after that time, 26DMP was favorably polymerized. These results indicated that the rate of the oxidation of 25DMP is slower than that of 26DMP. In other

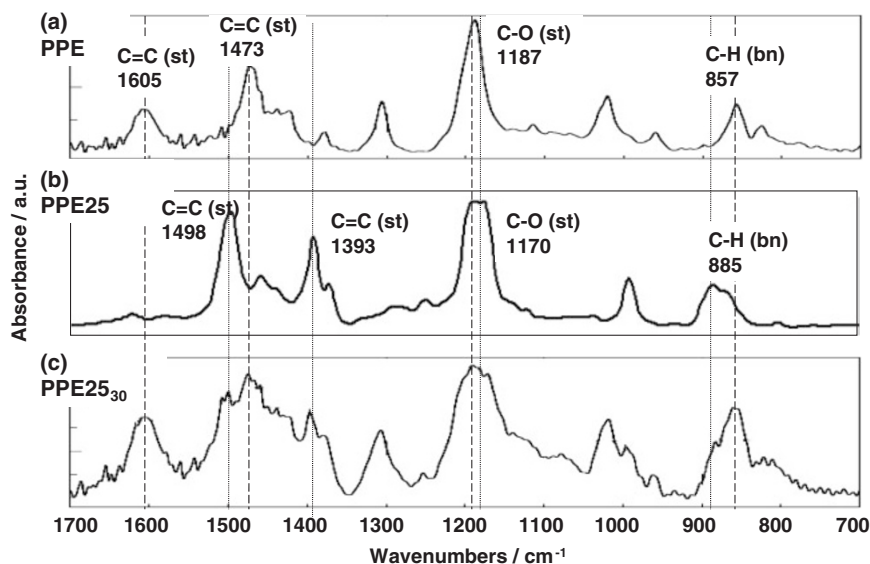


Figure 2. IR spectra of (a) sample 11 (PPE), (b) sample 1 (PPE25), and (c) sample 4 (PPE25₃₀). The dashed and broken lines indicate the absorption from PPE and PPE25, respectively.

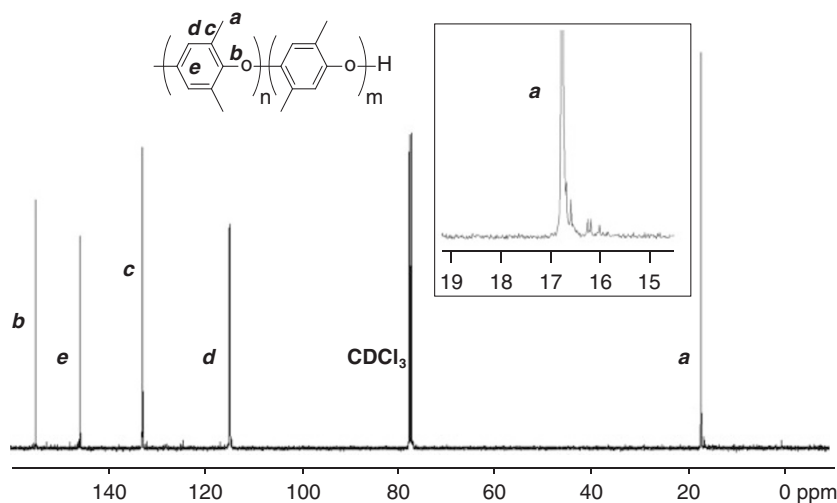


Figure 3. ¹³C NMR spectrum and expanded region (inset, 14–19 ppm) of sample 8 (PPE25₃).

words, 25DMP is more stable than 26DMP under the present oxidation conditions.

Characterization of the Copolymer

The structure of the copolymer was characterized by IR and NMR analysis. Figure 2 depicts the IR spectra of (a) PPE, (b) PPE25, and (c) PPE25₃₀. In the IR spectrum of the conventional PPE, absorption bands can be observed at 1473, 1187, 857 cm⁻¹, assignable to C=C stretching, C-O-C stretching, and C-H bending, respectively. In contrast, these bands were observed for PPE25 at 1498, 1170, and 885 cm⁻¹, respectively. The copolymer PPE25₃₀ has absorption bands corresponding to both PPE and PPE25 units, from which the composition of the two monomers in the copolymer was estimated to be about 62:38 (as calculated from C-H bending modes). Thus, the

composition of the copolymer can be controlled by the monomer feed ratio in copolymerization.

Because PPE25_x with a high molar ratio of 25DMP do not have sufficient solubility in CDCl₃, a PPE25_x sample of lower 25DMP content was selected for analysis by ¹³C NMR spectroscopy. Figure 3 depicts the spectrum of PPE25₃ and its expanded region (14 to 19 ppm) in CDCl₃ at 20 °C. Strong sets of signals are observed at 16.76, 114.2, 132.5, 145.4, 154.7 ppm, which are assignable to the 26DMP unit in the copolymer. In the expanded spectrum, smaller signals are observed at 16.67, 16.59, 16.24, 16.19, and 15.99 ppm. Since the ¹³C NMR spectrum of PPE25 shows methyl carbon signals at 16.2 ppm, the observation of these small signals indicates a plural sequence of 26DMP and 25DMP in the copolymer as shown in Figure 4.

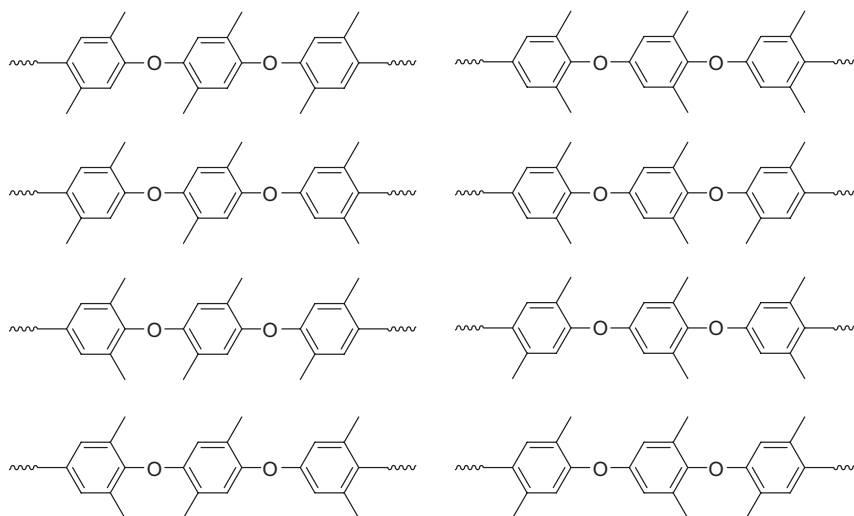


Figure 4. Possible sequences of the copolymer.

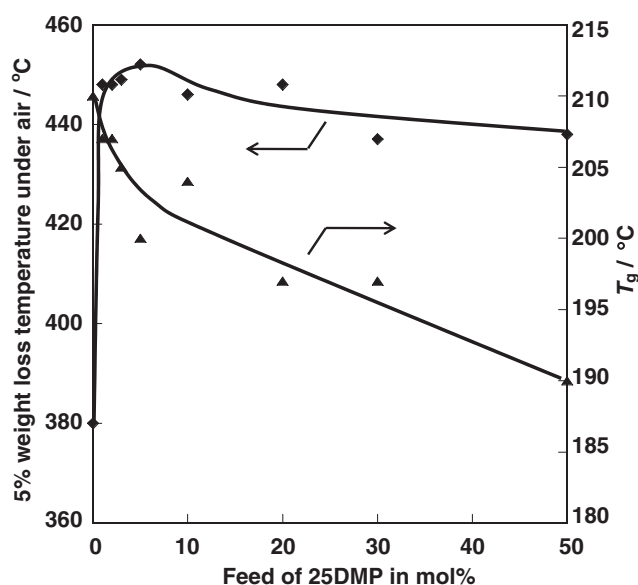
 Table II. Thermal properties of polymers PPE25_x^a

Sample	Abbreviation	T_g^b /°C	T_{d5}/Air^c /°C	T_{d10}/Air^c /°C	T_{d5}/N_2^c /°C	T_{d10}/N_2^c /°C
2	PPE25 ₇₀	183	402	426	406	421
3	PPE25 ₅₀	190	438	446	432	442
4	PPE25 ₃₀	197	437	446	439	446
5	PPE25 ₂₀	197	448	455	443	450
6	PPE25 ₁₀	204	446	451	442	446
7	PPE25 ₅	200	452	457	446	450
8	PPE25 ₃	205	449	452	444	448
9	PPE25 ₂	207	448	454	446	450
10	PPE25 ₁	207	448	454	444	445
11	PPE	210	380	401	430	441

^aPPE_x indicates the feed of 25DMP in *x*. ^bDetermined by DSC (N₂, 20 °C/min). ^cDetermined by TGA (N₂, 10 °C/min).

Thermal Stability

The thermal stability of the copolymer was investigated by TGA. Table II summarizes the results of the thermostability of the homo- and copolymers. It is noticeable that the inclusion of only 1 mol % of 25DMP significantly increased the thermostability to about 70 °C under air. Because both of the high reproducibility of this experimental result and the same isolation process of PPE and PPE25₁, the higher thermostability of PPE25₁ can be attributable to its nature, not the impurity. When the feed molar ratio of 25DMP was increased to 5 mol %, the thermostability of the copolymer attained a maximum value of 452 °C. Figure 5 shows the 5 wt %-loss temperature (T_{d5}) under air and the glass transition temperature of the copolymer plotted against the monomer feed ratio. The thermal stability of the copolymer sharply increases with an initial increase in the feed of 25DMP, and then gradually drops to 438 °C with further increases. As we already reported in literature, CuCl-TMEDA catalyst does not afford perfectly regio-controlled PPE25 homopolymer,¹⁵ the drop of thermostability in higher feed of 25DMP could be arisen by the unfavorable radical coupling site; C-C or C-O coupling at *ortho*


 Figure 5. T_{d5} and T_g of copolymers plotted against the feed composition of 25DMP.

position of OH moiety. In contrast, the glass transition temperature gradually decreases with increasing 25DMP, finally dropping to 190 °C for a 50 mol % feed of 25DMP, probably due to the shorter repeating number of the 26DMP unit in the copolymer. Thus, the copolymer could be processed at a lower temperature without the addition of another thermoplastic, which is generally required for conventional PPE in order to decrease its glass transition temperature sufficiently below the point of thermal decomposition.

TGA profiles of the conventional PPE (sample 11) and the copolymer PPE25₃ (sample 8) under air are shown in Figure 6. The value of T_{d5} of PPE, is 380 °C, which is 69 °C lower than that of PPE25₃. It is noticeable that the conventional PPE gains its weight at 278 °C by oxidation and reduces its weight from 358 °C, although no weight gain was observed for PPE25₃.

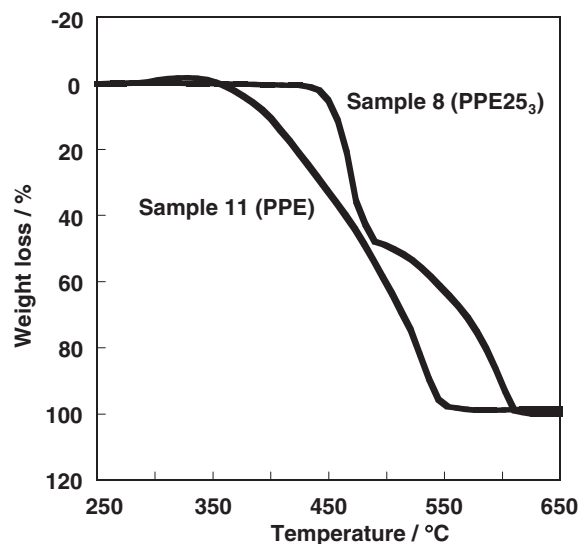


Figure 6. TGA profiles of (a) sample 11 (PPE) and (b) sample 8 (PPE_{25x}) (10°C/min under air).

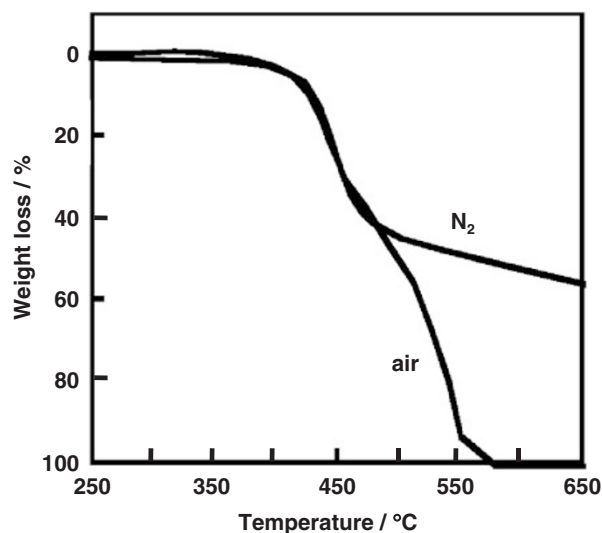


Figure 7. TGA profiles of PPE end functionalized with methyl iodide under air and nitrogen at a heating rate of 10°C/min.

Similar weight gain of PPE under air was also reported by A. Davis.¹⁷ The present results clearly indicate that copolymer has higher oxidation stability than PPE under air.

In order to determine the degradation mechanism of the copolymer, a fully end-functionalized PPE was prepared with methyl iodide. The value of T_{d5} of the as-prepared PPE (OH function at the terminal) was 380 and 430°C under air and nitrogen, respectively. In contrast, the TGA profiles of the end-functionalized PPE (OCH₃ function) under air and nitrogen are comparable and the T_{d5} was about 430°C in both cases. Pickett reported that the oxidation rate of the end capped PPE was lower than that of uncapped PPE.¹⁸ Based on these results and information from the literature, thermal decomposition of the PPE mainly could occur from the polymer end group under air and from the main chain under nitrogen (Figure 7).

Table III. Calculated total energy^a

Run	Substrates ^b	E_0^c /Hartree	ΔE^d /KJ mol ⁻¹
1	H	-0.502257	
2	26DMP	-386.2141	322.599
3	26DMP*	-385.5759	
4	26DMP-D	-771.2091	303.652
5	26DMP-D*	-770.5789	
6	25DMP	-386.2144	329.927
7	25DMP*	-385.5734	
8	25DMP-D	-771.2093	310.232
9	25DMP-D*	-770.5764	

^aCalculated by DFT method (B3LYP/6-311++G(d,p)). ^bThe abbreviation is as follows: H: hydrogen, 26DMP: 2,6-dimethylphenol, 26DMP*: 2,6-dimethylphenoxy radical, 26DMP-D: 2,6-dimethylphenol dimer, 26DMP-D*: 2,6-dimethylphenol dimer radical, 25DMP: 2,5-dimethylphenol, 25DMP*: 2,5-dimethylphenoxy radical, 25DMP-D: 2,5-dimethylphenol dimer, 25DMP-D*: 2,5-dimethylphenol dimer radical. ^cCalculated total energy. ^dDissociation energy of phenol derivatives into the radical species.

These results suggested that the high thermostability of PPE_{25x}, especially under air, is a result of the polymer end group, which could not be the 26DMP unit; thus, 25DMP mainly comprises the end units.

The higher stability of the copolymer with a 25DMP unit at the polymer chain end can be explained based on the dissociation energy, ΔE , of the OH group. To this end, the dissociation energy was estimated by a density functional theory (DFT) calculation (B3LYP/6-311++G(d, p) basis set). Table III summarizes the dissociation energy of the OH group in the monomeric and dimeric forms of 26DMP and 25DMP. In both cases, the dissociation energy, ΔE , of the 25DMP derivative is about 7 kJ/mol higher than that of the 26DMP derivative, implying a higher oxidation stability for the 25DMP unit. This estimation agrees well with the results of time-conversion curves by GC, in which 25DMP is more stable under oxidation conditions. One possible explanation of the higher thermal stability of the copolymers in comparison to that of PPE can be offered by the structure of the polymer end. If thermal degradation occurs from the polymer chain end, having the more thermostable 25DMP unit at the polymer end group should contribute to greater thermal stability overall. Therefore, the probability of having a 25DMP unit at the polymer chain end is much higher than that of 26DMP.

Mechanical Properties

Table IV summarizes the mechanical properties of the copolymer. Conventional PPE shows the tensile strength, tensile modulus, and the elongation at break to be 64 MPa, 2.9 GPa, and 3.8%, respectively. These values are improved to 80 MPa, 4.0 GPa, and 3.6% by copolymerization with 2 mol % of 25DMP. A further increase in the feed of 25DMP resulted in a decrease in the mechanical strength and the formation of a brittle film, probably as a consequence of the rigid-rod structure of the PPE₂₅ segment.

Digital camera images of the tested sample films are shown in Figure 8. Whereas conventional PPE was partially carbonized under the molding conditions (280°C, 5 MPa, 20 min),

Table IV. Mechanical properties of polymer^a

Sample	Abbreviation	Strength ^b /MPa	Modulus ^c /GPa	Elongation ^d /%
7	PPE25 ₅	67	3.3	3.4
8	PPE25 ₃	61	4.0	2.2
9	PPE25 ₂	80	4.0	3.6
10	PPE25 ₁	74	3.9	2.6
11	PPE	64	2.9	3.8

^aAll the films were molded at 5 MPa at 280 °C for 20 min. ^bTensile strength. ^cTensile modulus. ^dElongation at break.

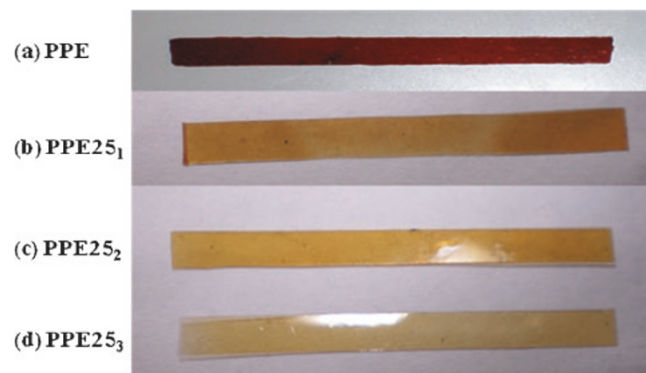


Figure 8. Digital camera images of the molded samples: (a) sample 11 (PPE), (b) sample 10 (PPE25₁), (c) sample 9 (PPE25₂), and (d) sample 8 (PPE25₃).

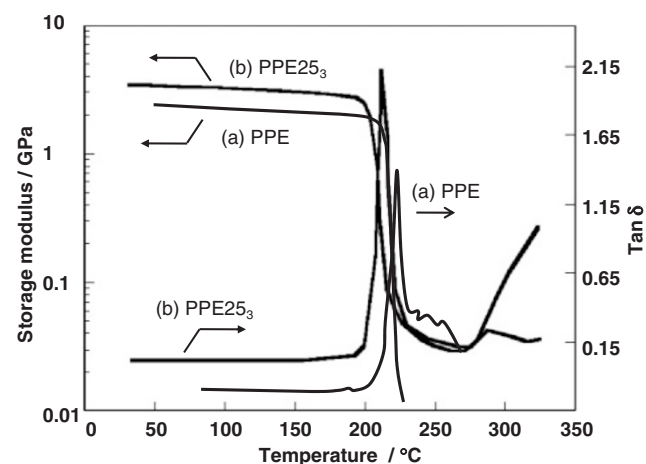


Figure 9. DMA profiles of (a) sample 11 (PPE) and (b) sample 8 (PPE25₃) (2 °C/min under N₂).

transparent films were obtained from copolymers ranging from PPE25₁ to PPE25₃. This result also supports the higher thermostability of the copolymer.

Figure 9 shows the DMA profile of (a) PPE (sample 11) and (b) PPE25₃ (sample 8). From the maximum of the $\tan \delta$ (E''/E') curve, the glass transition temperatures can be estimated at 222 and 212 °C, respectively, which is in good agreement with the values determined by DSC measurement. It is noticeable that the DMA profile of PPE drops abruptly after the glass transition temperature, but that of PPE25₃ recovers at 250 °C. After this temperature, the storage modulus E' of PPE25₃

Table V. Refractive index and dielectric properties of polymer

Sample	Abbreviation	n^a	ϵ (1 MHz) ^b	ϵ (10 GHz) ^c	Tan δ^c
7	PPE25 ₅	1.57	2.45	2.35	0.0066
9	PPE25 ₂	1.57	2.45	2.33	0.0032
10	PPE25 ₁	1.57	2.45	2.31	0.0043
11	PPE	1.57	2.45	2.38	0.0022

^aRefractive index at D-line by Abbe refractometer. ^bEstimated value at 1 MHz ($\epsilon = n^2$). ^cMeasured by cavity resonance method at 10 GHz.

rapidly increases, which suggests a crosslinking reaction occurs between the polymer chains probably because of the existence of the 25DMP unit. Although to specify the crosslinking point after gelation is difficult, the methylene coupling after the abstraction of benzyl proton of PPE25_x or the C-C/C-O coupling at ortho position of OH moiety of the 25DMP unit could be the most possible reaction.¹⁷

Refractive Index and Dielectric Properties

PPE offers potential as a next generation insulating material because of its excellent dielectric properties. Thus, to determine the influence of copolymerization with 25DMP on the dielectric properties, the refractive index (n), dielectric constant (ϵ), and dissipation factor ($\tan \delta$) were measured (Table V). All sample show a similar refractive index at around 1.57, and thus the estimated dielectric constant at 1 MHz ($\epsilon = n^2$) was almost the same. However, the dielectric constant at 10 GHz measured by the cavity resonance method was somewhat different among the polymers. That is, conventional PPE gave a dielectric constant of 2.38 as compared to a value of 2.31 for PPE25₁. The dielectric constant increases with the feed of 25DMP, which could be a result of the well-packed structure of the 25DMP repeating unit. The realization of improved thermal and mechanical properties of the copolymer while maintaining its low dielectric properties would expand the application of this material as a next generation low k insulator.

SUMMARY

2,5-Dimethylphenol was successfully copolymerized with 2,6-dimethylphenol using a di- μ -hydroxo-bis[$(N,N,N',N'$ -tetramethylethylenediamine)copper (II)]chloride catalyst in toluene under oxygen. The conversion of the two monomers was monitored by gas chromatography, which revealed that 25DMP was slightly less reactive than 26DMP. The resulting copolymers show a higher thermal stability of about 70 °C along with improved mechanical properties. This can be attributable to the 2,5-dimethylphenol unit, which is more likely to be located at the end of the copolymer.

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