Oxidative coupling copolycondensation of 2,6-dimethylphenol with 2,5-dimethylphenol: highly thermostable poly(phenylene ether)

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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] 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 (26DMP), 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. Very recently, a di-μ-hydroxo-bis[(N,N,N',N'-tetramethylethylenediamine)copper (II)]chloride (CuCl-TMEDA) catalyst was found to promote the regio-controlled oxidative polymerization of 2,5-dimethylphenol (25DMP) with base additive required (tetramethylethylenediamine 3 equiv to CuCl), although the regio-regularity was not perfect.[2] 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.

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 1 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),[3] 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 number-average molecular weight (M_n) value of around 10,000 is favorable. Thus, various copolymers (PPE25x, 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 by the monomer feed ratio, but the ratio of 25DMP in the copolymer gradually

Scheme 1: Copolymerization of 26DMP with 25DMP
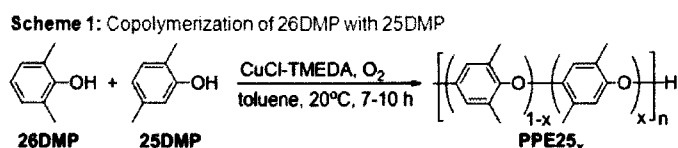
decreased in the high feed region (sample 2 and 3).

Characterization of the copolymer

The structure of the copolymer was characterized by IR and NMR analysis. 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 PPE25$_{30}$ 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.

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	PPE25-7	30:70	8	52	54:44	8,500	3.4
3	26DMP+25DMP	PPE25_60	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_22	80:20	7	61	86:14	7,800	2.3
6	26DMP+25DMP	PPE25_18	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

[a] Conditions: CuC(OH)/TMEDA 2.5 mol% b, TMEDA 10 equiv to copper ion, 20°C. [b] Determined by C-H wagging absorption in IR spectrum. [c] Determined by GPC (CHCl₃, PSt standard).

Because PPE25x with a high molar ratio of 25DMP do not have sufficient solubility in $CDCl_3$, a PPE25x sample of lower 25DMP content was selected for analysis by ^{13}C NMR spectroscopy. Figure 1 depicts the spectrum of PPE25₃ and its expanded region (14 to 19 ppm) in $CDCl_3$ 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 ^{13}C 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.
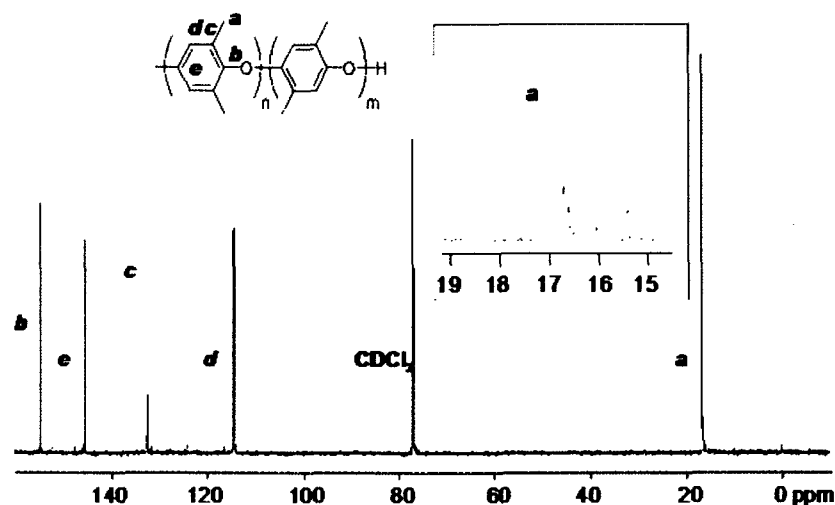
Figure 1. ^{13}C NMR spectrum and expanded region (inset, 14 – 19 ppm) of sample 8 (PPE25₃).

Thermal stability

The thermal stability of the copolymer was investigated by TGA. Table 2 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. 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,[3] 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 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

201C

the point of thermal decomposition.

In order to determine the degradation mechanism of the copolymer, a fully end-functionalized PPE was prepared with methyl iodide. The value of the 5 wt%-loss temperature (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 (OCH_3 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.[4] 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.

These results suggested that the high thermostability of PPE25x, 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.

Table 2. 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

[a] PPEx indicates the feed of 25DMP in x. [b] Determined by DSC (N_2, 20 °C/min). [c] Determined by TGA (N_2, 10 °C/min).

Mechanical properties

The mechanical properties of the copolymer were then investigated. 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.

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 δ) were measured. All sample show a similar refractive index at around 1.57, and thus the estimated dielectric constant at 1 MHz ($\varepsilon = n^2$) 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 PPE25$_1$. 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 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.

References and Notes
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