Copper-Catalyzed Regio-Controlled Oxidative Coupling Polymerization of 2,5-Dimethylphenol

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ABSTRACT: The regio-controlled oxidative coupling polymerization of 2,5-dimethylphenol using CuCl with 2-substituted pyridine ligands was investigated under an oxygen atmosphere. By increasing the bulkiness of the substituents of the pyridine, a higher molecular weight polymer was obtained with a good yield. CuCl with 2-phenylpyridine or 2-(*p*-tolyl)pyridine ligand yielded the corresponding poly(2,5-dimethyl-1,4-phenylene ether) polymer, which shows a melting temperature of around 310 °C. XRD indicated that these are semicrystalline polymers having a degree of crystallization of up to 42%.

Introduction

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) is one of the most widely used engineering plastics and is prepared by the oxidative coupling polymerization of 2,6-dimethylphenol in the presence of a copper−amine complex catalyst under an oxygen atmosphere.[1] PPE possesses excellent insulating and mechanical properties;[2−4] however, it has a relatively low glass-transition temperature of 210 °C and difficult processability. Unless extreme care is taken in the processing of PPE, thermooxidative degradation occurs, resulting in embrittlement of the molded specimen. Therefore, industrially, PPE is blended with polystyrene and rubber in order to decrease the processing temperature and improve its toughness, respectively.[5] Oxidative coupling polymerization is known to be an environmentally clean process because it catalytically proceeds under oxygen with the generation of water as a byproduct. Because the monomers that can be applied for the polymerization are limited to phenols with substituents on the 2- and 6-positions, an investigation of the regio-controlled oxidative coupling polymerization of phenols is required for developing a new engineering plastic. Recently, highly regio- or coupling-selectivity-controlled polymerizations with enzymatic and enzyme-model metal catalysts have been developed.[6] A typical enzymatic polymerization of phenol derivatives usually yields polymers containing phenylene (CC) units from 40 to 70%, which is dependent on the methanol/buffer ratio in the solution.[7] The CC coupling selectivity is improved up to 95% when poly(ethylene glycol) is added to the polymerization solution.[8] On the other hand, CO coupling predominantly occurs in the polymerization of phenol derivatives using tyrosinase model complexes.[9] Only a few reports have been published regarding the oxidative coupling polymerization of 2,5-dimethylphenol; most of these reports deal with regio-irregular polymers.[10] The tyrosinase model complexes was found to be effective for the regio-controlled oxidative polymerization of 2,5-dimethylphenol,[11] and later we reported that a copper complex immobilized within a mesoporous architecture was also useful to control the regio-regularity.[12] However, in order to realize an industrial-scale preparation, it is necessary to develop an elemental catalyst that functions more effectively. In the oxidative polymerization of phenol derivatives, the ligand of a copper catalyst is known to play an important role in controlling the coupling site; thus, we expect that the regio-regularity in the oxidative polymerization can be controlled by using ligands that are carefully selected according to the type of monomer. Here, we describe the oxidative coupling polymerization of 2,5-dimethylphenol using various copper−pyridine catalysts to achieve a predominant regio-regularity.

Experimental Section

Materials. All reagents and solvents were used without further purification.

Instrumentation. Gel permeation chromatography (GPC) was used to determine molecular weights M_n and molecular weight distributions, M_w/M_n, of polymer samples on Jasco GULLIVER 1500 equipped with a polystyrene gel column (Plgel 5 μm MIXED-C) eluted with chloroform at a flow rate of 1.0 mL min^{-1} calibrated by standard polystyrene samples. ^{1}H and ^{13}C NMR spectra of the polymers were obtained on a Bruker DPX-300 spectrometer at 300 MHz for ^{1}H and 75 MHz for ^{13}C measurement. Deuterated chloroform ($CDCl_3$) was used as a solvent with tetramethylsilane as an internal reference. Infrared (IR) spectra were recorded on a Horiba FT-720 spectrophotometer. Thermal analysis was performed on a Seiko EXSTAR 6000 DSC 6200 at a heating rate of 10 °C/min for differential scanning calorimetry (DSC) under nitrogen. X-ray diffraction (XRD) patterns were recorded on a Rigaku MiniFlex instrument. Polymer powders were placed on a glass plate for the measurement in the reflection mode with a scanning rate of 0.5° 2θ/min from 2 to 35° and Ni-filtered Cu Kα radiation from a 2kW Rigaku X-ray generator. A field emission scanning electron microscopic image (FE-SEM) was taken by a JSM7500-F at 15 kV accelerating voltage.

Polymerization. Typical procedure: Into a two-necked flask were added 0.0059 g (3 mol% to the monomer) of CuCl, 0.93 g (100 equiv to CuCl) of 2-phenylpyridine, and 3.3 mL of dichlorobenzene. The flask was purged with oxygen two times and stirred for 30 min. The polymerization was initiated by the addition of the monomer (0.244 g, 2.00 mmol) and the solution was vigorously stirred at 80 °C for 3 h. The resulting solution was poured into 50 mL of methanol containing 0.5 mL of concentrated hydrogen chloride to precipitate the polymer. The precipitate was collected, dissolved in chloroform, and reprecipitated with methanol. The polymer was collected and dried at 150 °C for 12 h under vacuum.

Results and Discussion

Hay reported that *o*-cresol was polymerized with several copper−2-substituted pyridines to yield a polymer with a high

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Scheme 1

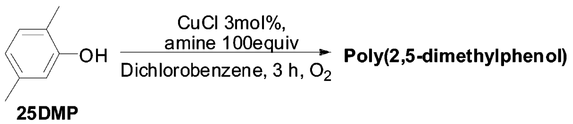

Table 1. Oxidative Polymerization of 2,5-Dimethylphenol with Various Copper−Amine Complexes[a]

run	ligand	temp, °C	yield, %[b]	M_n[c]	M_w/M_n[c]
1	pyridine	60	86 (gel)	d	d
2	2-picoline	60	89 (gel)	d	d
3	2,6-lutidine	60	82 (gel)[d]	d	d
4	2-propylpyridine	60	64	2700	2.5
5	2-phenylpyridine	60	78	3800	3.7
6[e]	2-(*p*-tolyl)pyridine	80	50 (insoluble)	f	f
7	2-benzylpyridine	60	6	1600	1.7
8	2,2′-dipyridyl	60	4	750	2.1

[a] Conditions: monomer 2 mmol, catalyst 3 mol %, amine 100 equiv added to CuCl, in dichlorobenzene, O_2 atmosphere, 3 h. [b] Methanol-insoluble part. [c] Determined by GPC (PSt, $CHCl_3$). [d] Gel was formed. [e] Polymerization time 6 h. [f] Insoluble polymer was obtained.

Table 2. Oxidative Polymerization of 2,5-dimethylphenol with a Cu−2-Phenylpyridine Complex[a]

run	catalyst, mol %	amine, equiv	temp, °C	time, h	yield, %[b]	M_n[c]	M_w/M_n[c]
1	3	100	40	3	62	3200	1.7
2	3	100	80	3	84	6300	7.8
3	3	100	80	6	91	8800	8.1
4	3	100	80	12	81 (gel)	d	d
5	2	100	80	3	34 (insoluble)	e	e
6	4	100	80	3	85 (gel)	d	d
7	3	50	80	12	84 (gel)	d	d
8	3	150	80	3	55 (insoluble)	e	e

[a] Conditions: monomer 2 mmol in dichlorobenzene, O_2 atmosphere. [b] Methanol-insoluble part. [c] Determined by GPC (PSt, $CHCl_3$). [d] Gel was formed. [e] Insoluble polymer was obtained.

inherent viscosity.[13] This result suggested that the longer substituents might efficiently block the coupling reaction at the *ortho* position. Therefore, we employed 2-substituent pyridines as a ligand of copper catalyst (Scheme 1). The results are summarized in Table 1. A copper−picoline catalyst or a copper−lutidine catalyst as well as a traditional copper−pyridine catalyst provided a brown gel (runs 1, 2, and 3). When 2-propylpyridine or 2-phenylpyridine was used as the ligand, a pale yellow polymer having a moderate molecular weight was obtained with a good yield. When the polymerization was performed with a copper−2-tolylpyridine catalyst, a chloroform-insoluble white powder was obtained. Other pyridine ligands such as 2-benzylpyridine and 2,2′-dipyridyl were not effective for this polymerization. Because 2-phenylpyridine provided the polymer with the highest yield, we selected this ligand for detailed study.

Table 2 summarizes the oxidative coupling polymerization of 2,5-dimethylphenol with the copper−2-phenylpyridine catalyst. By increasing the polymerization temperature, the yield of the polymer increased (runs 1 and 2). When the polymerization time was increased to 12 h at 80 °C, the polymerization solution became a gel, indicating cross-linking at the *ortho* position of the phenol derivatives (run 4). When the amount of the catalyst was increased, the rate of the polymerization increased, again resulting in a gel polymer (run 6). In contrast, an insoluble polymer was obtained in chloroform when a smaller amount of the catalyst was used (run 5). The amounts of 2-phenylpyridine used also affected the polymerization. Although the use of 50 equiv of the amine yielded a gel, a chloroform-insoluble polymer was obtained by adding 150 equiv of the amine to a copper salt (run 8). It is known that by decreasing the amount of catalyst or increasing the amount of amine additives, the C−C coupling reaction during the polymerization can be suppressed;[14] therefore, the insoluble polymer could be a crystalline structure due to a higher regio-regularity.

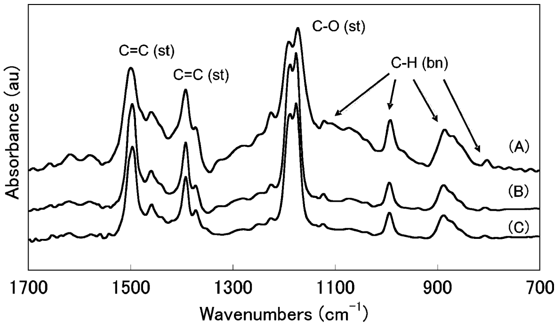

Figure 1. IR spectra of the polymers obtained by the conditions of (A) run 4 in Table 2, (B) run 5 in Table 1, and (C) run 8 in Table 2. Key: st, stretching; bn, bending.

To determine the regio-regularity, IR spectra of the typical (A) gel (run 4 in Table 2), (B) chloroform-soluble polymer (run 5 in Table 1), and (C) insoluble polymer (run 8 in Table 2) were measured, as shown in Figure 1. All the spectra show the characteristic absorptions of C═C stretching at 1500 and 1392 cm^{-1}, C−O−C stretching at 1176 cm^{-1}, C−H in-plane bending at 1122 and 1064 cm^{-1}, and out-of-plane bending at 887 and 806 cm^{-1}. In addition to these typical absorptions, small-to-medium absorptions are observed at around 1627, 1461, 1245, and 1064 cm^{-1} for A and B. The IR spectrum of C does not show these unclear absorptions; this indicates that pyridine derivatives with bulky ligands can inhibit the coupling at the *ortho* position of 2,5-dimethylphenol in mild conditions, yielding the corresponding linear polymer. It is considered that the solubility of the resulting polymer depends on the regio-regularity in the polymer chain.

^{1}H NMR spectra of these polymers were also taken to determine the regio-regularity (see Supporting Information). Two sharp signals that can be attributed to methyl and aromatic protons were observed at 2.20 and 6.64 ppm, respectively, with an integration ratio of 2:6 for the chloroform-soluble polymer. On the other hand, broad signals were observed in both areas for a polymer sample that was collected just before gelation, and the integration ratio was 2.0:6.7, indicating that the coupling reaction occurred at the *ortho* position as well as the *para* position during the polymerization.

Figure 2 shows the ^{13}C NMR spectra of the polymers obtained by the following conditions: (A) CuCl 3 mol %, pyridine/CuCl 100, 40 °C for 1 h and (B) run 3 in Table 2. In spectrum B, signals that can be attributed to the methyl and aromatic carbons were observed at 16.25 (*a*), 120.51 (*b*), 127.39 (*c*), and 151.23 (*d*) ppm, while very broad signals as well as unclear small signals were observed for the polymer obtained with the CuCl−pyridine catalyst. These spectra clearly indicate the formation of poly(2,5-dimethyl-1,4-phenylene ether) when the polymerization was conducted with the CuCl−2-phenylpyiridine catalyst. Therefore, it can be summarized that the copper−amine catalyst induces the polymerization of 2,5-dimethylphenol, and the production of a gel (regio-irregular), chloroform-soluble polymer (regio-regular), and chloroform-insoluble (highly regio-regular) polymer is primarily dependent on the amine ligand. The coupling at *ortho* position of 2,5-dimethylphenol was effectively suppressed by the use of pyridine derivatives with

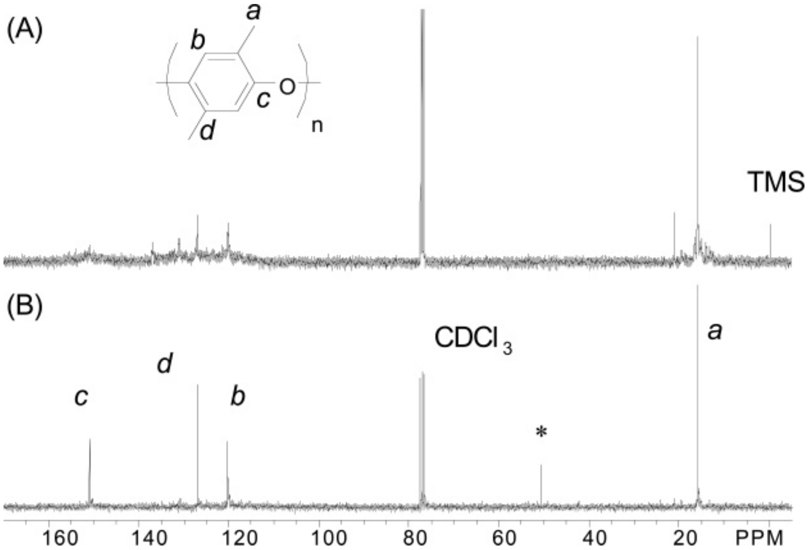

Figure 2. ^{13}C NMR spectra obtained by (A) CuCl-pyridine (40 °C for 1 h) and (B) CuCl-2-phenylpyridine (70 °C for 6 h). (∗) MeOH.

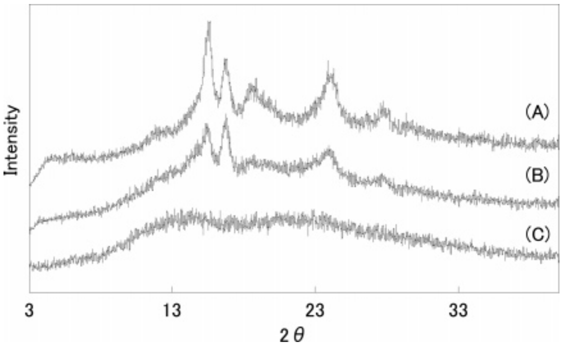

Figure 3. XRD patterns of the polymers obtained by the conditions of (A) CuCl 2 mol %, 2-tolylpyridine 100 equiv, 70 °C for 6 h, precipitated part, (B) run 5 in Table 2, and (C) run 5 in Table 1.

Table 3. Heat of Fusion and Degree of Crystallization of Poly(2,5-dimethyl-1,4-phenylene ether)[a]

run	CuCl, mol %	ligand	temp, °C	time, h	ΔH, J/g[b]	χ, %[c]
1	2	2-phenylpyridine	80	6	9.7	17
2	3	2-(*p*-tolyl)pyridine	60	6	17	22
3	3	2-(*p*-tolyl)pyridine	70	4.5	26	29
4[d]	3	2-(*p*-tolyl)pyridine	70	6	52	42

[a] Conditions: monomer 2 mmol in dichlorobenzene, O_2 atmosphere. [b] Heat of fusion. [c] Degree of crystallinity determined by XRD. [d] Only the polymer precipitated during the polymerization was isolated.

ortho-substituents (see Supporting Information). The amounts as well as the types of the amine additives could also play an important role to form a controlled phenoxy radical−copper complex, which might avoid the coupling at the open *o*-position of phenol derivatives.[9b]

To investigate the properties of these polymers, thermal analyses were conducted by differential scanning calorimetry (DSC) (see Supporting Information). A chloroform-insoluble polymer (run 5 in Table 2) shows a broad endothermic peak due to melting at around 310 °C, while no peak was observed for the chloroform-soluble and gel samples. The broad melting behaviors could be induced by recrystallization during the polymerization, in which the solution was vigorously mixed in the presence of catalyst residues at a high temperature. The enthalpy of the melt varied from 10 to 26 J/g, which is lesser than that of poly(*p*-phenylene ether) (84 J/g) whose melting point is 252−272 °C.[15] These results indicated that the regio-regularity of the polymer was dependent on the type of the pyridine ligand used for the polymerization, resulting in a semicrystalline polymer.

To confirm these experimental results, we performed XRD analyses for these polymer samples. Figure 3 depicts the profiles of the samples, in which an insoluble polymer shows strong peaks at 2θ values of 15.54, 16.68, 18.50, 23.86, and 27.66. These values were transformed into *d* values of 5.698, 5.311, 4.792, 3.726, and 3.222 Å, respectively. Table 3 summarizes the heat of fusion (ΔH) and the degree of crystallinity (χ) of the resulting polymers. All samples were insoluble with any organic solvent (even with concentrated sulfonic acid or *o*-dichlorobenzene at 140 °C); thus, their molecular weights were

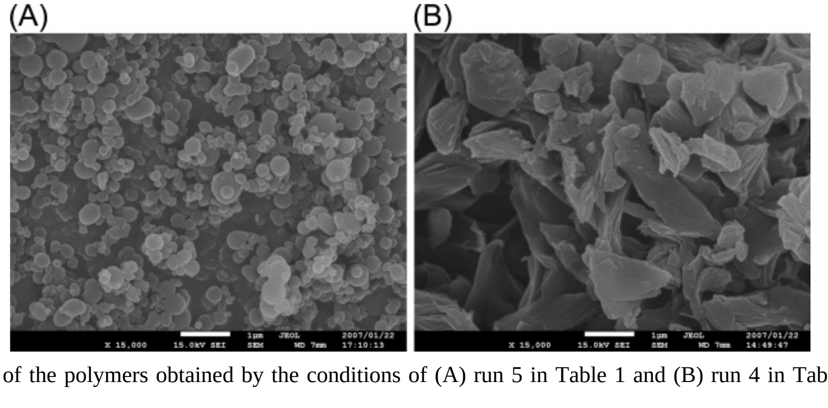

Figure 4. FE-SEM images of the polymers obtained by the conditions of (A) run 5 in Table 1 and (B) run 4 in Table 3.

not evaluated. Tolylpyridine was more effective than phenylpyridine for controlling the regio-regularity, and the ΔH values varied from 10 to 26 J/g. Since the highly regio-regular polymer was precipitated during the polymerization, the precipitate was only collected to evaluate its structure. This white powder was washed with chloroform several times, dried, and the χ value was found to be 42 J/g. Therefore, only the highly crystalline polymer was precipitated during the polymerization; the polymer with medium-to-high crystallinity was still in the solution so that the overall χ value was lowered.

Figure 4 shows a representative SEM image of the (A) chloroform-soluble polymer and (B) chloroform-insoluble polymer. The insoluble polymer shows a large platy structure that is approximately 4 μm along the long axis, while a much smaller sphere mass with a diameter of 0.2 μm is observed in the soluble polymer.

Conclusions

We investigated the regio-controlled oxidative coupling polymerization of 2,5-dimethylphenol using CuCl-2-substituted pyridine catalysts under oxygen. By increasing the bulkiness of the substituents on the *ortho* position of the pyridine, a higher molecular weight polymer was obtained without gel formation. CuCl−2-tolylpyridine was the most effective ligand for controlling the regio-regularity, resulting in the corresponding semicrystalline polymer.

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Supporting Information Available: Figures showing the ^{1}H NMR spectra of polymers, DSC profiles, and the optimized geometry of catalysts by using TD−DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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