Oxidative Coupling Polymerization of Substituted Phenols with a Copper Amine Catalyst Immobilized within Mesoporous Silica

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Summary: SBA-15-supported CuCl catalyst was prepared for the regio-controlled oxidative polymerization of phenol derivatives. The solid-supported catalyst was fully characterized by X-ray, elemental analysis, TEM observation, and nitrogen absorption-desorption experiment, and CuCl was found to be uniformly immobilized in the mesopores. This catalyst was employed for the oxidative polymerization of 2,5-dimethylphenol and *o*-cresol, resulting in excellent regio-selectivity during the polymerization.

Keywords: catalyst; controlled polymerization; mesoporous silica; oxidative polymerization; poly(aryl ether)

Introduction

Poly(phenylene ether)s (PPEs) are attractive materials for engineering plastics, and are produced by oxidative coupling polycondensation catalyzed by the copper-amine complexes under oxygen.[1] Substituent groups on 2,6-position of phenolic OH moiety are necessary to prevent formation of unfavorable branching polymers, limiting the availability of phenols for polymer synthesis.[2] Here, we present the preparation of a novel mesoporous-supported Cu-amine catalyst and the oxidative polymerization of 2,6-dimethylphenol, 2,5-dimethylphenol, and *o*-cresol.

Experimental

Materials

CuCl was dissolved in concHCl, filtered, and diluted with distilled water. The precipitate was collected, and washed subsequently with methanol and ether. Finally this was dried at 100 °C for 12 h under the reduced pressure. *o*-Dichlorobenzene was distilled over P_2O_5 under nitrogen. Pyridine was distilled from K_2CO_3 under nitrogen. 2,5-Dimethylphenol was purified by sublimation. Other reagents and solvents were used as received. SBA-15 was synthesized by using P123 [poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymer $M_{avg.} = 5800$ $EO_{20}PO_{70}EO_{20}$] as a template. 2.0 g of P123 triblock copolymer was dissolved in the mixture of 45.0 g of water and 30.0 g of 4 M HCl. To this solution was added TMOS (tetramethyl orthosilicate) as silica source at 40 °C. The solution was stirred for 20 h at the same temperature, and the mixture heated at 80 °C for 24 h. The solid product was collected by filtration and dried at room temperature in air. The template was removed by calcination in air at 550 °C for 6 h. *N,N,N'*-Trimethyl-*N'*-[3-(trimethoxysilyl)-propyl]ethylenediamine was prepared according to the literature.[3] Cu was loaded onto the SBA-15 by dispersing in 2-methoxyethanol under air for 24 h. The organic component in SBA-15 was evaluated to be 15.81% from the combustibles in its elemental analysis, and the Cu ion

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concentration was determined to be 1.92 mmol per 1 g of SBA-15 catalyst from the ICP analysis. After functionalization, the hysteresis loop of the isoterm was shifted to lower P/P_0 and mesopore volume were decreased. After functionalization, BJH pore-size, BET surface decreased from 8.2 to 6.0 nm, from 813 to 344 m^2/g. The shape of hysteresis loop didn't changed before and after functionalization, indicating that functionalization of SBA-15 has uniformly pores. SEM image exhibits fiber-like particles about 100 nm. TEM observation reveals the formation of 1D cylindrical mesopore with uniform size. It is obvious that the specific mesoporous structure has advantage to produce the shape-controlled polymer. As a porous silica without regulated hole size, silica gel for HPLC grade (BET surface area ca 500 m^2/g, 70–230 mesh, 60 Å) was obtained from Aldrich, and the CuCl loading was similarly performed described in SBA-15-supported catalyst.

Measurement

^1H and ^{13}C NMR spectra were obtained on a BRUKER DPX-300 spectrometer at 300 MHz for ^1H and 75 MHz for ^{13}C measurement. Deuterated chloroform ($CDCl_3$) was used as a solvent with tetramethylsilane as an internal standard. 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 a flow rate of 1.0 mL min^{-1} calibrated by standard polystyrene samples. X-ray diffraction (XRD) patterns were obtained on with Cu Kα radiation (PHLIPS X'Pert-MPD PW3050) N_2 adsorption-desorption isotherms were measured by SA-3100 systems, and pore-size distributions were determined by Barrett-Joyner-Halenda (BJH) method.

Polymerization

Typical procedure is as follows; Into a flask filled with oxygen were added copper catalyst, 5 mL of dry solvent, and amine as an additive. The heterogeneous solution was stirred for 5 min at the set temperature, and then the polymerization was initiated by charging 3 mmol of monomers. After the set time, the polymerization solution was poured into methanol containing concentrated HCl, the precipitate was collected diluted by filtration, washed with methanol, and dried in vacuo at 100 °C for 12 h.

Results and Discussion

SBA-15-Supported Catalyst[3]

Copper ion was incorporated into SBA-15 silica materials by functionalization of SBA-15 with *N,N,N′*-trimethyl-*N′*-trimethoxysilylpropyl ethylenediamine. The molar ratio of diamine and Si in SBA-15 with a diamine functionality (without Cu) was determined by elemental analysis to be 0.9:13. After immobilization of Cu ions, the ratio of Cu to Si was estimated by inductively coupled plasma atomic emission spectroscopy (ICP) and elemental analysis as 1.0:13, indicating similar formation of copper and diamine. X-ray diffraction (XRD) analysis of SBA-15 before and after the modification showed second and third peaks in addition to the first strong peak, indicating that a regular nano-structure was maintained during the modification. A nitrogen absorption-desorption study showed a clear hysteresis loop of the isotherm even after diamine modification. Pore diameter before and after the modification was 8.20 and 6.00 nm, respectively, as estimated by the Barrett-Joyner- Halenda (BJH) method. In addition, BET surface areas decreased from 813 to 344 m^2/g, respectively. These results revealed that copper ions are immobilized homogeneously on the internal surface of the SBA-15 material.

Oxidative Polymerization of 2,6-Dimethylphenol[3]

The well-characterized SBA-15-supported catalyst was then employed for the oxidative polymerization of 2,6-dimethylphenol.

The polymerization was performed using 2mol% of the Cu-catalyst in the presence of pyridine (160 equiv to Cu) in toluene at 20 °C under oxygen for 12 h. The monomer was quantitatively converted into the polymer in 100 min, while it took 130 min for the conventional homogeneous Cu-amine catalyst (CuCl-pyridine) as shown in Figure 1. This may be explained by the concentrated Cu catalyst within the mesoporous channel, and by the spontaneous movement of the hydrophilic phenolic monomer into the channel from the hydrophobic toluene phase. After the quantitative conversion, the M_n increased as the polymerization time and the polydispersity index (PDI) became 2.2. In contrast, the homogeneous catalyst gave the polymer with higher M_n, but the PDI was over 10, indicating the advantage of the mesoporous-supported catalyst.

Oxidative Copolymerization of 2,6-Dimethylphenol with 2-Allyl-6-Methylphenol

We reported the copolymerization of 2,6-dimethylphenol with 2-allyl-6- methylphenol for a novel thermosetting resin with low dielectric constant, but the PDI increased with the polymerization time.[4] We believed this might attribute to the formation of branching unit during the polymerization. The PDI was around 30 when the polymerization of 2,6- dimethylphenol and 2-allyl-6-methylphenol (9/1 in molar ratio) was performed with 2mol% of the CuCl-pyridine catalyst at 40 °C for 3 h. In contrast, the mesoporous-supported catalyst gave the copolymer with a reasonable PDI of 2.5. Thus, the branching was effectively supressed by the limited polymerization space of the mesoporous material.

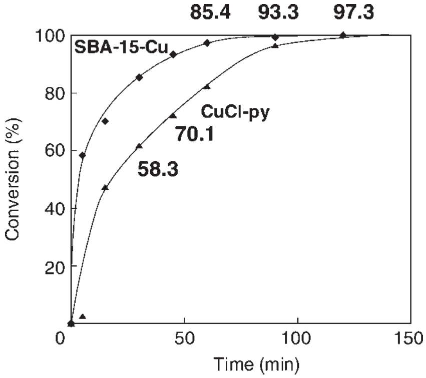

Figure 1.
Time-conversion curves of 2,6-dimethylphenol by SBA-15-supported catalyst and the conventional homogeneous catalyst. Conditions; monomer 3 mmol, catalyst 2 mol%, solvent toluene/pyridine 5/1 (mL/mL), oxygen atmosphere.

The ^{1}H NMR spectrum of the resulting copolymer was depicted in Figure 2. In addition to the signals at 2.09 and 6.47 ppm assignable to methyl and aromatic protons, respectively, of the polymer main chain, signals assignable to vinyl and allyl protons were observed at 5.84, 5.00, and 3.20 ppm, respectively, indicating the successful copolymerization of two monomers.

Oxidative Polymerization of 2,5-Dimethylphenol[5]

PPE is a commercially available engineering plastic, which is prepared by the oxidative polymerization of 2,6-dimethylphenol. Introduction of 2,6-substituents are necessary to obtain a linear polymer, which limits the availability of the monomers in this polymerization. Several reports on oxidative polymerization of 2,5-dimethylphenol were published, but it is generally difficult to prepare the linear polymer except for the polymerization with a sterically hindered Cu-amine catalyst.[6] We expected that the mesoporous-supported catalyst would be effective to realize the regio-controlled polymerization because of the limited polymerization space inside the channel. The polymerization was conducted with 3 mol% of the Cu catalyst in the presence of 2-propylpyridine as an additive at 90 °C for 12 h in dichlorobenzene under oxygen. The M_n and PDI of the resulting polymer was 4,400 and 2.3, respectively, and the polymer was not soluble in toluene at 25 °C at the concentration of 0.01g/mL. In contrast, CuCl-2-propylpyridine catalyst gave gel at 70 °C, and the HPLC glade silica gel-supported Cu catalyst gave also gel at 90 °C. The expanded ^{13}C NMR spectra of

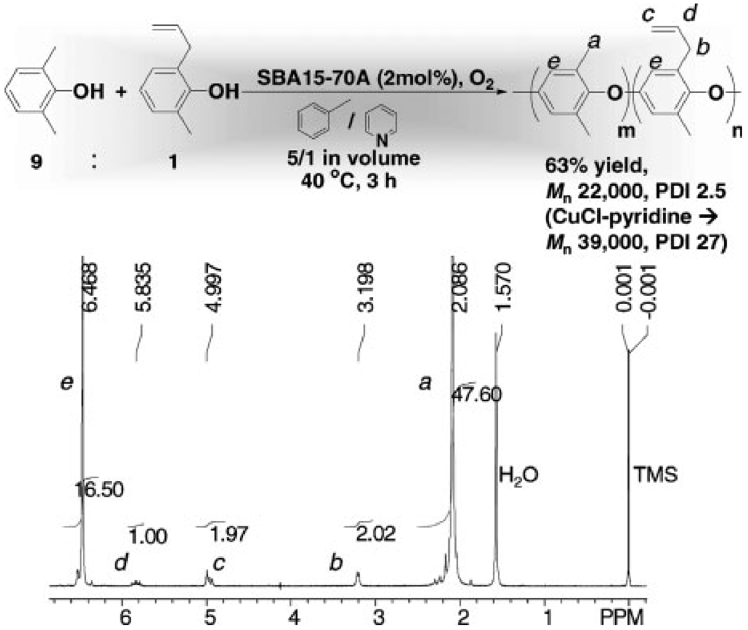

Figure 2.
^{1}H NMR spectrum ($CDCl_3$, PSt Std) of the copolymer obtained by the oxidative polymerization of 2,6-dimethylphenol with 2-allyl-6-methylphenol. Conditions; 2.7 mmol of 2,6-dimethylphenol, 0.3 mmol of 2,allyl-6-methylphenol, 2 mol% of SBA-15-supported catalyst in toluene/pyridine (5/1 mL/mL) at 40 °C for 3 h under oxygen.

the polymers prepared with a) homogeneous CuCl-2-propylpyridine catalyst at 40 °C for 1 h ($M_n = 6300$, PDI = 17) and b) SBA-15-supported catalyst ($M_n = 4400$, PDI = 2.3) are shown in Figure 3. While only weak broad signals were observed in Figure 3a, a single signal assignable to methyl carbon in the corresponding linear polymer was observed at 15.84 ppm in Figure 3b, indicating that almost perfect regio-selectivity was realized in the mesoporous channnel.

Oxidative Polymerization of *o*-Cresol

Cresols are a widely occuring natural group, and used for household cleaners and disinfectant. However, they are not suitable to polymerize by oxydative polymerization because of the absence of a subsituent on 6-position. Thus, almost all efforts did not succeed in the preparation of the corresponding linear polymer. Although the bulky copper-amine catalysts are able to be close to the reasonable PDI index, the attainable M_n decreased with the bulkiness (Table 1). The expanded ^{13}C NMR spectrum of the polymer obtained by the CuCl-2-2ropylpyridine catalyst is shown in Figure 4a. Signals at 16.4 and 16.2 ppm were assignable to the methyl carbon in the

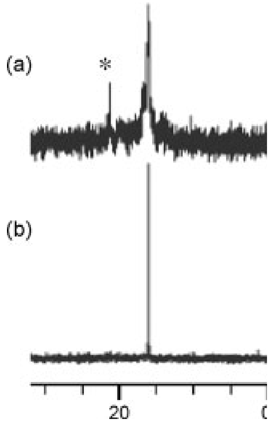

Figure 3.
Expanded ^{13}C NMR spectra of poly(2,5-dimethylphenol). *toluene.

Table 1.
Oxidative polymerization of *o*-cresol with Cu-amine catalyst.[a)]

Run	Amine	M_n[b)]	PDI
1	pyridine	2400	22.7
2	2-butoxypyridine	4300	43.5
3	2-propylpyridine	5900	5.9
4	2-phenylpyridine	1500	3.4
5	dipyridyl	1300	2.3
6	bipicoline	800	2.0

[a)] Polymerization was conducted using 3 mmol of the monomer, 2 mol% of CuCl in toluene/amine (100 equiv to CuCl) at 90 °C for 3 h under oxygen.
[b)] Determined by GPC ($CHCl_3$, PSt Std).

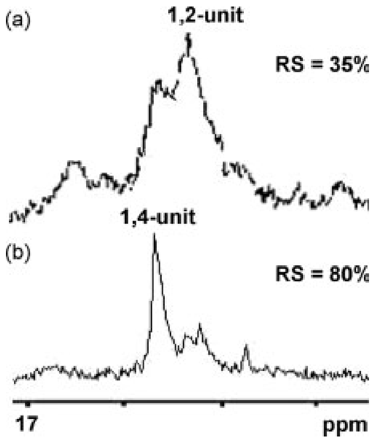

Figure 4.
Expanded ^{13}C NMR spectra of poly(*o*-cresol) obtained by a) CuCl-2-propylpyridine and b) SBA-15-supported catalyst under the same conditions described in Table 2.

corresponding linear polymer and that in the branching unit, respectively. As the results, the regio-selectivity can be roughly calculated to be 35%.

Table 2 summarize the results of the polymerization using the mesoporous-supported catalyst with various additives. The maximum regioselectivity of 80% was obtained when the polymerization was performed using 1 mol% of the catalyst in the presence of 2-phenylpyridine (100 equiv to Cu) at 90 °C for 24 h under oxygen. The expanded ^{13}C NMR spectrum of the resulting polymer is depicted in Figure 4b. While many unknown peaks were observed in Figure 4a, such small unknown signals were disappeared and the intensity of the signal at 16.4 ppm corresponding to the 1,4-linkage of the polymer increased, indicating that the mesoporous interior effectively supressed the formation of unfavorbale branching polymer.

Conclusion

As a summary, we prepared a novel mesoporous supported Cu-amine catalyst and demonstrated oxidative polymerization of phenol derivatives. Poly(2,6-dimethyl-1,4-phenylene ether) with controlled PDI was obtained with the SBA-15-supported catalyst, and the copolymer with 2-allyl-6-methylphenol was obtained as well. Regio-controlled polymerization of

Table 2.
Oxidative polymerization of *o*-cresol with SBA-15-supported catalyst.[a)]

Run	Amine	Temp/°C	M_n[b)]	PDI[b)]	Yield[c)]/%	RS[d)]/%
1	pyridine	60	-	-	trace	-
2	pyridine	90	-	-	gel	-
3	2-butoxypyridine	90	5000	2.4	22.0	70
4	2-hexyloxypyridine	90	2700	1.2	0.5	-
5	2-phenylpyridine	90	4100	1.5	36.2	80
6	dipyridyl	90	4200	1.4	10.2	78
7	bipicoline	90	-	-	quinone	-
8	phenanthoroline	90	-	-	quinone	-

[a)] Polymerization was conducted using 3 mmol of the monomer, 2 mol% of the catalyst in toluene/amine (100 equiv to CuCl) for 3 h under oxygen.
[b)] Determined by GPC ($CHCl_3$, PSt Std).
[c)] Methanol insoluble part.
[d)] Determined by the integrated ratio of 1,4- and 1,2-unit in ^{13}C NMR (Figure 4).

2,5-dimethylphenol and *o*-cresol was realized by the SBA-15-supported catalyst, which will be used for the variety of regiocontrolled polymerization of other phenol derivatives as well.

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