

Oxidative Coupling Polymerization of 2,6-Dimethylphenol with a Copper–Amine Catalyst Immobilized within the Interior of SBA-15

Yuji Shibasaki, Masahiro Nakamura, Ryuhei Ishimaru,[†] Junko N. Kondo,^{*,†,††} and Mitsuru Ueda

Department of Organic & Polymeric Materials, Graduate School of Science & Engineering, Tokyo Institute of Technology, 2-12-1-H120 O-okayama, Meguro-ku Tokyo 152-8552

[†]Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuda-cho, Midori-ku, Yokohama 226-8503

^{††}New Energy and Industrial Technology Development Organization

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An effective method to control polydispersity (M_w/M_n) in the oxidative coupling polymerization of 2,6-dimethylphenol has been developed. SBA-15 functionalized with *N,N,N'*-trimethyl-*N'*-trimethoxysilylpropylethylenediamine and copper chloride(I) produced a polymer with the number average molecular weight (M_n) of 44000 and M_w/M_n of 3.9, when the polymerization was conducted in toluene/pyridine (5/1 volume ratio) at 40 °C for 12 h under oxygen atmosphere. The conventional catalytic system [CuCl(I)–pyridine] afforded the polymer with M_n of 81000 and M_w/M_n of 40, indicating the effectiveness of the mesoporous catalyst.

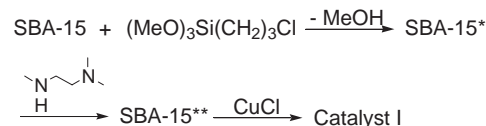
Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) constitutes a class of macromolecules known as engineering thermoplastics,¹ which possess excellent properties such as high toughness, dimensional stability, good flame retardation, and low moisture uptake. However, due to their high thermal stability (glass transition temperature T_g near 215 °C), a high processing temperature is usually required, resulting in partial degradation of the PPE. Because T_g is affected by the molecular weights of polymers, relatively low molecular weight PPE [number average molecular weight (M_n) from 10000 to 30000] is generally utilized commercially to minimize problems during processing.² PPE is produced industrially by oxidative coupling polymerization (OCP) of 2,6-dimethylphenol (26DMP) catalyzed with a copper salt.³ Depending on the structure of amines and copper salts, and other reaction conditions such as oxygen pressure, the rate of OCP and product yield are significantly affected⁴ by side reactions such as the formation of Mannich-base-type end groups⁵ and PPE with two OH functional groups caused by the redistribution of 3,3',5,5',-tetramethyl-4,4'-diphenoquinone (TMDPQ).⁶ Oxidative coupling polymerization of 26DMP usually produces broad polydispersities (M_w/M_n) or multimodal profiles from gel permeation chromatography (GPC), probably because of branching by chain transfer reactions.⁷ Thus, a new method is needed to control M_w/M_n during PPE synthesis. A PPE with a narrow M_w/M_n (1.7 to 2.2) was prepared by precipitation polymerization of 26DMP using a mixed solvent of isopropanol and toluene, but the maximum M_n of the resulting PPE was limited to 7500.⁸ A PPE with a very narrow M_w/M_n of 1.07 was prepared utilizing trimer-redistribution reaction in dichloromethane with TMDPQ as an initiator.⁹ The complex of PPE with dichloromethane was formed within two weeks, resulting in an M_n of only 1700. Phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol using an oxidative initiator such as lead oxide or potassium ferricyanide led to branching and failed to produce

a high M_n PPE.¹⁰ Percec et al. developed an efficient phase transfer catalytic system for PPE synthesis, in which M_n and its OH functionality could be controlled, but reported poor yields in low M_n PPE syntheses and multimodal M_w/M_n .¹¹

We recently reported the regio-controlled polycondensation of 2,5-dimethylphenol using a copper-amine catalyst on SBA-15, resulting in almost complete regio control by the mesoporous interior.¹² This OCP in the mesoporous interior also would be useful for the control of M_w/M_n and prevention of chain transfer reactions. In this article, we describe a convenient and efficient method for the formation of PPEs with M_w/M_n controlled by the mesoporous interior.

SBA-15 was prepared according to the reported procedure.¹³ The pore size and BET surface areas were estimated as 7.1 nm and 590 m²/g, respectively, using the Barrett–Joyner–Halenda (BJH) method. The modification of SBA-15 with 3-chloropropyl-trimethoxysilane was performed in toluene at 100 °C for 12 h. The resulting solid was purified with a soxhlet condenser using hot toluene for 5 h. The white solid was dried and characterized by elemental analysis. The ratio between Si and Cl was 10:1 as determined by elemental analysis. Then, *N,N,N'*-trimethylethylenediamine was reacted with the modified SBA-15 at 150 °C for 6 h under nitrogen. After washing with hot toluene using a soxhlet condenser for 12 h, the resulting white product was dried at 100 °C for 12 h in vacuum. Nearly complete modification of the diamine function was observed, as indicated by a Si:diamine moiety ratio of 10:1.1, determined by elemental analysis. Finally, the coordination of the copper salt was performed using two equiv. of copper chloride(I) to diamine group in 2-methoxyethanol at 25 °C for 24 h under air. Excess amounts of copper salt were removed by washing with hot pyridine, and the resulting blue powder was collected and dried in vacuum at 100 °C for 12 h. Concentration of the copper salt was determined by inductively coupled plasma atomic emission spectroscopy (ICP) analysis to be 0.84 mmol/g for catalyst I. The pore size was 6.0 nm.

Oxidative coupling polymerization of 26DMP was conducted using 2 mol % of copper catalyst at 20–60 °C for 12 h under oxygen atmosphere. Table 1 summarizes the results of the polymerization. A conventional CuCl(I)–pyridine catalyst provided PPE with M_n of 63000 and M_w/M_n of 10.6 at 20 °C. Increasing



Scheme 1. Preparation of SBA-15 catalysts.

Table 1. Polymerization of 2,6-dimethylphenol (26DMP)^a

Entry	Catalyst	Temp/°C	Yield /% ^b	M_n^c	M_w/M_n^c
1	CuCl	20	86	63000	10.6
2	CuCl	40	92	81000	40.0
3	I	20	85	49000	2.2
4	I	40	83	44000	3.9

^aConditions; monomer 3 mmol, catalyst 2 mol %, solvent toluene/pyridine 5/1 (mL/mL), 12 h, oxygen atmosphere.

^bIsolated by filtering and precipitation with methanol.

^cDetermined by GPC (PSt, CHCl₃).

polymerization temperature to 40 °C dramatically increased the M_w/M_n value to 40, indicating that the oxidative coupling polymerization was accompanied by side reactions such as branching at the benzyl position and redistribution reactions, which frequently occur at this temperature. In contrast, catalyst I provided a PPE with M_w/M_n of 2.2 at 20 °C, and 3.9 at 40 °C.

To study this type of polymerization in detail, time-conversion relationships were plotted as shown in Figure 1. Rapid monomer conversion was observed compared to a conventional CuCl–pyridine catalyst under oxygen. This may be attributed to the concentration of the catalytic site in the narrow mesoporous interior and the spontaneous flow of the monomer into the more polar mesoporous channel from the less polar toluene solution after 26DMP interaction with pyridine.

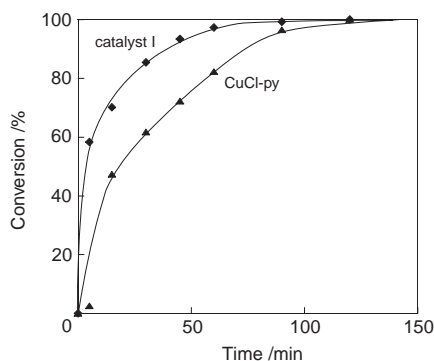
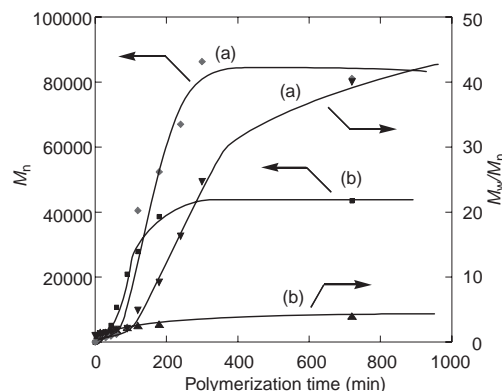
**Figure 1.** Time-conversion curves by catalyst I.

Figure 2 depicts M_n and M_w/M_n vs polymerization time at 40 °C (Entries 2 and 4 in Table 1). M_n and M_w/M_n values for the resulting polymers increase with polymerization time in both systems, however, a more rapid increase in M_n was observed in the mesoporous polymerization until 100 min. After that, a maximum of 44000 was observed, and a reasonable M_w/M_n value of 3.9 is observed. A rapid M_n increase is consistent with that of quick monomer conversion, as seen in Figure 1. In contrast, the conventional CuCl–pyridine catalytic system provided a polymer with higher M_n with very large M_w/M_n value. The difference in M_n values between conventional and mesoporous systems can be explained by the limited space within a mesoporous material, where reactions between large molecules such as oligomers would be controlled. It is notable that the M_w/M_n of the polymer obtained by a conventional catalyst dramatically increased with polymerization time because of branching, but this undesirable phenomenon was not central in the mesoporous system. The T_g values of these polymers were analyzed by differential scanning calorimetry at a flow rate of 20 °C/min under nitro-

**Figure 2.** M_n , M_w/M_n vs polymerization time (min) plots for the polymerization with a) conventional CuCl–pyridine system (Entry 1, Table 1) and b) mesoporous catalyst (Entry 3, Table 1).

gen, which yielded similar T_g values near 220 °C on a second heating from 100 to 280 °C. The ¹H and ¹³C NMR spectra of these polymers were quite similar; therefore, the large difference in M_w/M_n values may be attributed to a small amount of branching and redistribution of the polymer chain.

In summary, we demonstrated the effectiveness of a Cu–amine catalyst immobilized on mesoporous material SBA-15 for the oxidative coupling polymerization of 26DMP. The rate of monomer conversion was rapid, and the M_w/M_n of the resulting polymer was below 3.9 at 40 °C for 12 h, whereas a conventional catalytic system provided a polymer with the very large M_w/M_n of 40.

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