Macromolecules

Volume 37, Number 26 December 28, 2004

Communications to the Editor

Regiocontrolled Oxidative Coupling Polycondensation of 2,5-Dimethylphenol Induced by Mesoporous Interior

Yuji Shibasaki,[†] Masahiro Nakamura,[†] Ryuhei Ishimaru,[‡] Junko N. Kondo,[*,‡] Kazunari Domen,[‡] 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, Japan, and
Chemical Resources Laboratory, Tokyo Institute of
Technology, 4259 Nagatsuda-cho, Midori-ku,
Yokohama, Kanagawa, 226-8503, Japan

Received August 28, 2004
Revised Manuscript Received October 28, 2004

Poly(phenylene ether)s such as poly(2,6-dimethyl-1,4-phenylene ether) and poly(2,6-diphenyl-1,4-phenylene ether) 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 the 2,6-position of the phenolic OH moiety are necessary to prevent formation of unfavorable branching polymers, limiting the availability of phenols for polymer synthesis.[2] Hay et al. reported that catalysts involving CuCl with 2-alkylpyridine such as 2-tridecylpyridine were effective for the synthesis of high-molecular-weight poly(2,5-dimethylphenol);[3] however, branching could not be completely excluded. Recently, Higashimura et al. reported a successful catalyst μ-η^2:η^2-peroxo dicopper(II) complex in conjunction with a bulky 2,6-diphenylpyridine base for the regiocontrolled synthesis of poly(2,5-dimethyl-1,4-phenylene ether) having an average molecular weight (M_n) of 4000 and molecular weight distribution (M_w/M_n) of 4.9.[4] They applied this catalytic system to the polymerization of other phenols such as *o*-cresol[5] and *m*-cresol;[6] however, no clear evidence of regioregularity except for the IR spectroscopic study exists. Nevertheless, these results suggest that the careful design of the catalytic environment is vital for achieving regioselectivity in phenol polymerization.

Mesoporous materials, developed in 1992, have unique structures with regulated hole size from 2 to 50 nm and are utilized in various fields such as material chemistry, adsorption processes, and catalysis.[7] Organic−inorganic hybrid materials based on such a mesoporous material are attractive, and one of the successful materials is an organic wire of a conductive polymer such as polyaniline[8] or carbon nanowires[9] from the pyrolysis of polyacrylonitrile or polyphenylene vinylenes. Characteristics of the compounds resulting from polymerization in mesoporous materials have also been reported. The gas-phase polymerization of α-olefin, vinyl acetate, styrene, and methyl methacrylate within MCM-41 produced polymers with unusual properties in degree of branching,[10] glass transition temperatures (T_g),[11] molecular weights,[12] and stereospecificity.[13] High crystallinity resulted from ethylene[14] and 1,4-diethynylbenzene[15] polymerizations using the distinctive properties of MCM-41 nanointerior. These results indicate that the nanosurrounded space in mesoporous materials restrict the formation of branching and cross-linking in polymerizations. This effect would be also useful to control the regioselectivity in oxidative coupling polymerization of phenols.

Here, we demonstrate a new method to control regioregularity of the oxidative coupling polymerization of 2,5-dimethylphenol utilizing a copper−amine catalyst immobilized on mesoporous material, which prevents the formation of branching and cross-linking in the polymerization.

Copper ion was incorporated into SBA-15 silica materials by functionalization of SBA-15 with *N,N,N′*-trimethyl-*N′*-trimethoxysilylpropylethylenediamine, prepared by condensation of *N,N,N′*-trimethylethylene-

---

[*] To whom all the correspondence should be addressed: Tel (+81)-45-924-5282; Fax (+81)-45-924-5238; e-mail jnomura@res.titech.ac.jp.

[†] Graduate School of Science and Engineering.

[‡] Chemical Research Laboratory.

10.1021/ma0482361 CCC: $27.50

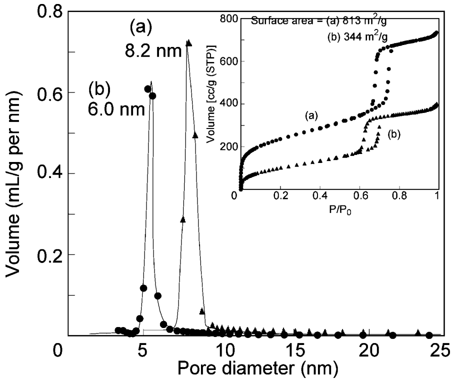
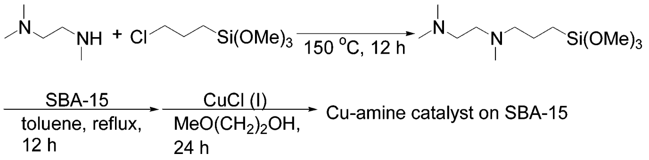


Figure 1. N_2 gas adsorption−desorption isotherms (inset) and pore size distribution of (a) SBA-15 (triangle) and (b) functionalized SBA-15 (filled circle). Pore size distribution was calculated using BJH analysis.

Scheme 1. Synthesis of Mesoporous Catalyst



diamine and trimethoxysilylpropyl chloride with heating (at 150 °C for 6 h), repeated immersion in CuCl(I) solution in 2-methoxyethanol at 20 °C for 24 h, followed by the removal of excess Cu ion by washing with pyridine as shown in Scheme 1.[16]

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 nanostructure was maintained during the modification. A nitrogen absorption−desorption study showed a clear hysteresis loop of the isotherm even after diamine modification as shown in Figure 1. 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.

Using this well-characterized mesoporous catalyst at a ratio of 3.3 mol % to the monomer, the polymerization of 2,5-dimethylphenol was performed in *o*-dichlorobenzene at 70 and 90 °C for 12 h under an oxygen atmosphere (Table 1). An off-white powder was obtained in 22 and 56% yield at 70 and 90 °C, respectively, by precipitation in MeOH containing a few drops of 12 N HCl in water (runs 3 and 4). M_n and M_w/M_n values were 4300 and 1.6 and 4400 and 2.3, respectively, as determined by GPC ($CHCl_3$ at 40 °C, PSt standards), whereas a conventional catalyst provided a brown polymer with a large M_w/M_n value of 17 at 40 °C for 1 h and insoluble material at 70 °C (runs 1 and 2). It is notable that the M_n and M_w/M_n values obtained by the mesoporous catalyst are comparable with and smaller than that in the literature (M_w/M_n = 4.9), respectively.[4] To confirm the effect of nanointerior modification, a Cu catalyst immobilized on porous silica was prepared[17] and used for the oxidative polymerization of 2,5-dimethylphenol. The polymerization at 90 °C yielded only insoluble material, suggesting the occurrence of gel formation due to the uncontrolled regioselective coupling (run 5).

Table 1. Oxidative Polymerization of 2,5-Dimethylphenol[a]

run	catalyst	temp (°C)	yield (%)	M_n[b]	M_w/M_n[b]
1[c]	CuCl	40	34	6300	17
2	CuCl	70	gel		
3	SBA-15−CuCl	70	22	4300	1.6
4	SBA-15−CuCl	90	56	4400	2.3
5	silica−CuCl[d]	90	gel		

[a] Polymerization conditions: monomer 3 mmol, catalyst 3 mol %, 2-propylpyridine 1 mL, *o*-dichlorobenzene 5 mL, O_2 atmosphere, 12 h. [b] Determined by GPC (PSt standard, $CHCl_3$, 40 °C). [c] Polymerization time 1 h. [d] Cu catalyst on porous silica.[19]

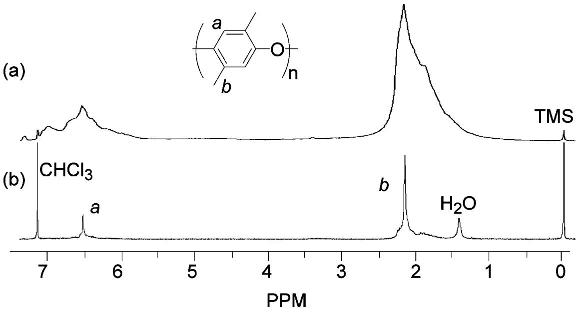


Figure 2. ^1H NMR spectra ($CDCl_3$ at 55 °C) of poly(2,5-dimethylpehnol) obtained by (a) conventional CuCl−2-propylpyridine (run 1 in Table 1) and (b) SBA-15 catalyst at 90 °C (run 4 in Table 1).

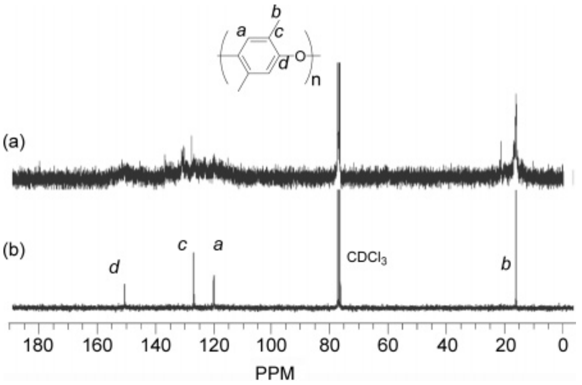


Figure 3. ^{13}C NMR spectra ($CDCl_3$ at 55 °C) of poly(2,5-dimethylpehnol) obtained by (a) conventional CuCl−2-propylpyridine (run 1 in Table 1) and (b) SBA-15 catalyst at 90 °C (run 4 in Table 1).

Figures 2 and 3 depict ^1H and ^{13}C NMR spectra of polymers obtained by (a) conventional CuCl(I) with 2-propylpyridine catalyst at 40 °C for 1 h (run 1 in Table 1) and (b) a catalyst on SBA-15 at 90 °C for 12 h (run 4 in Table 1). Two sharp signals at 2.2 and 6.6 ppm with small peaks assignable to terminal units are shown in Figure 2b, while very broad signals are shown in Figure 2a. Four sharp signals assignable to methyl (*b*) and aromatic carbons (*a, c, d*) were clearly observed at 16.21, 120.46, 127.47, and 151.22 ppm, respectively, as shown in Figure 3b, whereas additional small signals can be seen in Figure 3a. To clarify the regioselectivity, the ^1H NMR spectrum of the polymer obtained in run 5 of Table 1 was studied. The polymer, obtained in a shorter period (10 h) in the conditions, was soluble in $CHCl_3$, and the

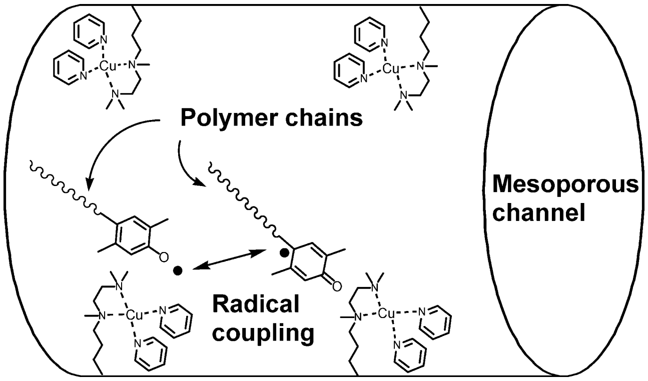


Figure 4. Plausible mechanism for 2,5-dimethylphenol polymerization using SBA-15 catalyst.

^{1}H NMR spectrum of this showed poor regioselectivity as seen in the polymerization with conventional CuCl–amine catalyst. These results indicate that the copper–amine catalyst promoted the oxidative coupling polymerization of 2,5-dimethylphenol and that regioselective coupling was strictly induced by the interior of the mesoporous channel of SBA-15, as shown in Figure 4.

Differential scanning calorimetry (DSC) was then taken to study the thermal property of the resulting polymer. An endothermic peak corresponding to its melting point was observed at 320 °C in the second scan, indicating the fine regioselectivity of the polymer.

In conclusion, we synthesized a novel copper–amine catalyst immobilized on mesoporous material (SBA-15) and characterized the regiocontrolled oxidative coupling polymerization of 2,5-dimethylphenol in solution. Reaction was performed between *N,N,N′*-trimethylethylenediamine having trimethoxysilyl functionality and SBA-15. The functionalized SBA-15 was then treated with CuCl(I), giving the mesoporous catalyst, which consisted of Cu, diamine, and Si in a molar ratio of 0.9:1.0:13, as determined by elemental and ICP analyses. The oxidative coupling polymerization of 2,5-dimethylphenol with this catalyst provided the regiocontrolled 1,4-polymer, when polymerization was conducted in *o*-dichlorobenzene in the presence of 2-propylpyridine at 90 °C for 12 h under an oxygen atmosphere. This novel approach to control regioregularity is a powerful tool for the synthesis of phenol polymers, useful for engineering new plastics.

Acknowledgment. The authors thank Dr. M. Tokita (Departmento of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology) for measuring the DSC. This work was supported by Industrial Technology Research Grant 2003 from NEDO (New Energy and Industrial Technology Development Organization) of Japan (ID 03A23010c).

References and Notes

(1) Hay, A. S. *Prog. Polym. Sci.* **1999**, *24*, 45.

(2) Jachowicz, J.; Kryszewski, M.; Sobol, A. *Polymer* **1979**, *20*, 995.

(3) Hay, A. S.; Endres, G. F. *Polym. Lett.* **1965**, *3*, 887.

(4) Higashimura, H.; Fujisawa, K.; Moro-oka, Y.; Namekawa, S.; Kubota, M.; Shiga, A.; Uyama, H.; Kobayashi, S. *Macromol. Rapid Commun.* **2000**, *21*, 1121.

(5) Higashimura, H.; Fujisawa, K.; Moro-oka, Y.; Kubota, M.; Shiga, A.; Uyama, H.; Kobayashi, S. *J. Mol. Catal. A: Chem.* **2000**, *155*, 201.

(6) Higashimura, H.; Fujisawa, K.; Moro-oka, Y.; Kubota, M.; Shiga, A.; Uyama, H.; Kobayashi, S. *Appl. Catal. A: Gen.* **2000**, *194*, 427.

(7) Tajima, K.; Aida, T. *Chem. Commun.* **2000**, *24*, 2399. Hashimoto, T. *Polym. Yearbook* **2000**, *17*, 367. Kageyama, K.; Ng, S. M.; Ichikawa, H.; Aida, T. *Macromol. Symp.* **2000**, *157*, 137. Stein, A. *Adv. Mater.* **2003**, *15*, 763. Stein, A.; Melde, B. J.; Schroden, R. C. *Adv. Mater.* **2000**, *12*, 1403.

(8) Wu, C.-G.; Bein, T. *Stud. Surf. Sci. Catal.* **1994**, *84*, 2269. Colomban, Ph.; Efremova, A.; Regis, A.; Vendange, V.; Gruger, A.; Badot. J. C. *Microporous Mater.* **1995**, *4*, 65.

(9) Moriguchi, I.; Koga, Y.; Yasuhiro, R.; Teraoka, Y.; Kodama, M. *Chem. Commun.* **2002**, *17*, 1844. Hlavaty, J.; Rathousky, J.; Zukal, A.; Kavan, L. *Carbon* **2000**, *39*, 53.

(10) Pelrine, B. P.; Schmitt, K. D.; Vartuli, J. C. US Patent, 19931214, 1993.

(11) Llewellyn, P. L.; Ciesla, U.; Decher, H.; Stadler, R.; Schueth, F.; Unger, K. *Stud. Surf. Sci. Catal.* **1994**, *84*, 2013.

(12) Ng, S. M.; Ogino, S.; Aida, T.; Koyano, K. A.; Tatsumi, T. *Macromol. Rapid Commun.* **1997**, *18*, 991.

(13) Tudor, J.; O'Hare, D. *Chem. Commun.* **1997**, *6*, 603.

(14) Kageyama, K.; Aida, T. *Science* **1999**, *285*, 2113.

(15) Lin, V. S.-Y.; Radu, D. R.; Han, M.-K.; Deng, W.; Kuroki, S.; Shanks, B. H.; Pruski, M. *J. Am. Chem. Soc.* **2002**, *124*, 9040.

(16) SBA-15 was synthesized using P123 [poly(ethylene oxide)$_{20}$-*b*-poly(propylene oxide)$_{70}$-*b*-poly(ethylene oxide)$_{20}$ $M_n = 5800$ $EO_{20}PO_{70}EO_{20}$] as a template. 2.0 g of P123 triblock copolymer was dissolved in a mixture of 45.0 g of water and 30.0 g of 4 M HCl. To this solution was added tetramethyl orthosilicate as a silica source at 40 °C. The solution was stirred for 20 h and then heated at 80 °C for 24 h. A solid product was collected by filtration and dried at room temperature in air. The template was removed by calcinations in air at 550 °C for 6 h. *N,N,N′*-Trimethyl-*N′*-trimethoxysilylpropylethylenediamine was prepared by condensation of *N,N,N′*-trimethylethylenediamine and trimethoxysilylpropyl chloride at 150 °C for 12 h and purified by vacuum distillation (62% yield); bp 65 °C/0.1 mmHg. ^{1}H NMR ($CDCl_3$, δ, ppm): 3.57 (s, 9H), 2.33–2.48 (m, 6H), 2.24 (s, 9H), 1.59 (m, 2H), and 0.62 (t, 2H). ^{13}C NMR ($CDCl_3$, δ, ppm): 61.29, 57.57, 55.65, 50.58, 45.96, 42.58, 20.24, and 6.79. Anal. Calcd for $C_{11}H_{28}N_2O_3Si$: C, 49.96%; H, 10.67%; N, 10.59%. Found: C, 49.99%; H, 10.72%; N, 11.02%.

(17) Cu catalyst on porous silica was prepared by previously published method^{16} using silica gel (70–230 mesh, 60 Å, BET surface area ~ 500 m^2/g, Aldrich Chemicals) for column chromatography as a matrix.

MA0482361