New Manganese Catalyzed Regiocontrolled Synthesis of Poly(2,5-dialkyl-1,4-phenylene oxide)s

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ABSTRACT: A new catalyst system is developed for regiocontrolled synthesis of poly(2,5-dialkyl-1,4-phenylene oxide)s by oxidative coupling polymerization of 2,5-dialkylphenol. The treatment of the α-benzoin oxime with manganese chloride in methanol under basic condition led to the formation of manganese benziloxime complex in which α-benzoin oxime was converted to benziloxime and coordinated to manganese as bidentate ligands. The polymerizations were conducted in toluene using manganese benziloxime complex and dibutylamine in a continuous flow of oxygen, and the structures, properties of the catalyst, and polymers were studied by nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and gel permeation chromatography (GPC). The catalyst showed high regioselectivity and reasonably good yields to afford the poly(2,5-dimethyl-1,4-phenylene oxide)s with 1,4-C-O linkage structure which possessed melting point higher than the poly(p-phenylene sulfide) or type II liquid crystalline polymer. The regioselectivity was enhanced when employing molecular sieves-supported manganese catalyst system at 90°C and the crystallinity of poly(2,5-dimethyl-1,4-phenylene oxide)s was estimated by wide-angle X-ray scattering (WAXS) and DSC. The crystallinity was calculated about 23.7% and a heat-reversible melting and crystallization behavior occurred at 327.8 and 306.8°C, respectively. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1501–1507, 2009

Key words: catalysts; crystallization; high temperature materials; metal-organic catalysts/organometallic; poly (phenylene oxide)

INTRODUCTION

Catalytic oxidative polymerization of 2,6-disubstituted-phenol is one of the most important methods of producing linear phenolic-derived polymers with high heat resistance and low dielectric constant.[1,2] Among the various dialkylpoly(phenylene ether)s, only poly(2,6-dimethyl-1,4-phenylene ether) has been successfully commercialized and widely used in electrical appliance due to its excellent physical and chemical properties. Studies concerning the preparation, characterization, and property of poly(2,6-dialkyl-1,4-phenylene ether) have been widely reported in the literatures, however, little work has been carried out for the synthesis of poly(2,5-dialkyl-1,4-phenylene ether).[3–7] This is probably because the conventional copper/amine catalyst system exhibited poor regioselectivity for ortho-unsubstituted phenols,[3,4] and an undesired tar was usually obtained due to branching or crosslinking reactions at ortho-positions. Previous work in controlling the regioselectivity of ortho-unsubstituted phenol derived polymers employed tyrosinase model complexes, in which (hydrotris(3,5-diphenyl-1-pyrazolyl)borate) copper complex (Cu(Tpzb)) and (1,4,7-triisopropyl-1,4,7-triazacyclononane) copper complex (Cu(L^{iPr})) were used as catalysts to polymerize 4-phenoxyphenol,[5] o-cresol,[6] and m-cresol[7] in a regiospecific manner. Studies by Higashimura suggested that a μ-η^2 : η^2-peroxo dicopper(II) species formed in the reaction resulted in the "radical-controlled" oxidative polymerization of ortho-unsubstituted phenols. Recently, Kondo et al. reported a regiocontrolled synthesis of poly(2,5-dimethyl-1,4-phenylene ether) using copper-amine catalyst immobilized on mesoporous SBA-15 silica materials which inferred that nanosurrounded space in mesoporous materials restrict the formation of branching and crosslinking in polymerizations.[8] Other researchers have also shown that a semicrystalline poly(2,5-dimethyl-1,4-phenylene ether) can be synthesized by using CuCl with 2-phenylpyridine or 2-(p-tolyl)pyridine ligand.[9] Reviewing all these studies, most catalysts, however, involved complicate preparation procedures which appeared unlikely to be employed in industrial process or other applications. Thus, the aim of our work is to provide a convenient method for regiocontrolled synthesis of poly(2,5-dialkyl-1,4-phenylene

oxide)s using manganese benziloxime complex and dibutylamine as the catalysts for oxidative coupling polymerization.

EXPERIMENTAL

Materials

All reagents and solvents were reagent grade. 2,5-dimethylphenol (2,5-DMP) was obtained from Alfa Aesar (Karlsruhe, Germany) and recrystallized from methanol before use. α-benzoin oxime and 2,6-dimethylphenol (2,6-DMP) were purchased from ACROS (Geel, Belgium). Manganese (II) chloride tetrahydrate, 2,5-diisopropylphenol (2,5-DIPP), dibutylamine (DBA), and sodium hydroxide were purchased from Aldrich Chemicals (St. Louis, MO) and used as received. Chloroform, toluene, methanol, and hexane were purchased from Mallinckrodt (Phillipsburg, NJ). Ethylenediaminetetraacetic acid disodium salt solution (EDTA) was purchased from Scharlau Chemie (Barcelona, Spain). Molecular sieves $(Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] xH_2O, 4Å$, grain size 2 mm) was purchased from Riedel-de Haën (Seelze, Germany).

Characterization

^1H and ^{13}C NMR spectra were recorded on a 300 and 75 MHz Varian-Mercury$^+$ 300 spectrometer using the CDCl$_3$ solvent and the internal standard tetramethylsilane. Fourier transform infrared spectroscopy (FTIR) spectra were recorded for KBr disks using a Perkin-Elmer Spectrum One spectrometer in the optical range of 400–4000 cm^{-1} with a resolution of 2 cm^{-1}. The molecular weight of the polymers was determined by gel permeation chromatography (GPC) which was carried out with polymer solutions in tetrahydrofuran (THF). Samples were prepared at nominally 1 mg ml^{-1} in THF and injected by Waters 717 autosampler. GPC system (Waters 515 high performance liquid chromatography pump, 1 mL/min, 40°C) was equipped with Waters Styragel HR0.5, HR4E, and HR5 and a Waters model 2410 refractive-index detector. The molecular weights were calibrated with polystyrene molecular weight standards (molecular weight = 500–370,000, SM-105, Shodex Japan). Differential scanning calorimetry (DSC) measurements were performed on a DSC Q10 differential scanning calorimeter (TA Instruments). The instrument was calibrated with high purity indium as standard. Samples of about 5 mg were weighed into aluminum pans that were hermetically sealed for standard DSC analysis. The nitrogen gas flow was 50 mL/min. Thermogravimetric analysis was performed with a TGA Q50 (TA instrument) thermogravimetric analyzer under nitrogen atmosphere.

Samples (10– 15 mg) were brought into platinum pans and put in the oven at 30°C. Heating scans carried out from 30 to 800°C at 20°C/min. Nickel was used for calibration. The temperatures of 5 wt % weight loss were determined. Wide-angle X-ray diffraction (WAXS) of the polymer was carried out with Shimadzu XRD-6000 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) for 2θ angle of 10°–50° operating at 40 kV and 30 mA. Oxidation potentials of 2,5-DMP, 2,5-DIPP, and 2,6-DMP were measured on a CHI 611C electrochemical workstation (Austin, TX) using a three-electrode cell assembly consists of an screen printed electrode as working electrode, a silver reference electrode, and a carbon auxiliary electrode. The disposable screen printed carbon electrode (TE100-BI) was purchased from Zensor R&D (Taichung, Taiwan). The test solutions were prepared by mixing 5–10 mL of $1.25 \times 10^{-4}M$ isopropyl solution with equal amount of 0.1M KCl/HCl buffer solution (pH = 2) and scanned at a rate of 0.1 V s^{-1} from −0.8 to +0.8 V for both reductive and oxidative windows.

General procedure for the preparation of catalyst

To a stirred solution of MnCl$_2$•4H$_2$O (1.05 g, 5.31 mmol) in 40 mL of methanol was added α-benzoin oxime (2.4 g, 10.56 mmol). After stirring for 10 min, the mixture was added 50% NaOH aqueous solution (1.0 g, 12.50 mmol) and the solvent was slowly evaporated by stirring for 24 h at room temperature and then dried at 60°C for 12 h in oven. The molecular sieves-supported manganese catalyst was prepared by incipient wetness impregnation technique: 0.21 g of the MnCl$_2$•4H$_2$O and 0.48 g of α-benzoin oxime was dissolved in 10 mL of methanol for 15 min and subsequently were added about 8 g of the molecular sieves and 0.2 g of 50% NaOH aqueous solution. The amount of solvent was just enough to cover the molecular sieves and the solvent was slowly evaporated for 24 h to afford the molecular sieves-supported manganese catalyst. After the solvent was evaporated, the sample was dried at 60°C for 2 h.

General procedure for the preparation of poly(2,5-dialkyl-1,4-phenylene oxide)s

To a stirred solution of manganese benziloxime complex (0.5 g) in 25 mL of toluene at 90°C was added 0.2 g (1.55 mmol) of dibutylamine. The mixture was added slowly with 2,5-dimethylphenol (1.6 g, 13.11 mmol) and 0.4 g (5.0 mmol) of 50% NaOH aqueous solution. The reaction temperature was kept at 90°C with a continuous oxygen flow through the reaction mixture for 7 h. The insoluble solid was filtrated and the solution was washed with 40 mL 1.2N HCl solution, twice with 4 mL portion of 0.2N EDTA

<div align="center">

TABLE I
Synthesis and Analysis of the Poly(2,5-dialkyl-1,4-phenylene oxide)s

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1. a. R = CH$_3$
    b. R = CH(CH$_3$)$_2$
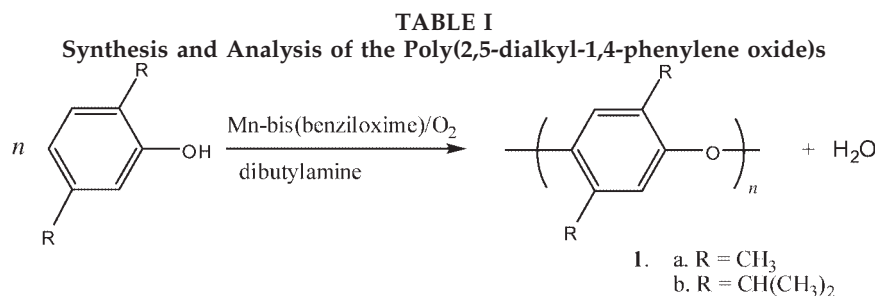
Entry	R	Catalyst system	Temp (°C)	Time (h)	Yield[a] (%)	$T_{d5\%}$ (°C)	Char[b] (%)	M_n	M_w
1	CH$_3$	Mn-benziloxime	25	5	48	372	47.7	12449	78978
2	CH$_3$	Mn-benziloxime	90	7	52	373	26.6	4222	8508
3	CH$_3$	Mn-benziloxime/molecular sieves[c]	25	2	36	382	38.5	6789	16734
4	CH$_3$	Mn-benziloxime/molecular sieves[c]	90	8	18	389	41.3	3225	5107
5	CH(CH$_3$)$_2$	Mn-benziloxime	25	7	59	335	5.9	5556	15448
6	CH(CH$_3$)$_2$	Mn-benziloxime	90	7	34	328	5.4	3209	5046
7	CH(CH$_3$)$_2$	Mn-benziloxime/molecular sieves[d]	90	14	13	290	23.2	5064	6154

[a] Calculated for isolated methanol-insoluble part polymers after purifications.
[b] Char residue (wt % at 800°C).
[c] 8 g of catalyst was employed, DBA (1.6 mmol), 2,5-DMP (13.11 mmol).
[d] 3 g of catalyst was employed, DBA (0.77 mmol), 2,5-DIPP (2.84 mmol).

solutions, and twice with 60 mL portion of deionized water. The polymer was precipitated by dropwise addition into a 10-fold excess of stirred methanol. The polymer was purified by dissolving in chloroform and reprecipitated in a 15-fold excess of stirred methanol. The precipitated polymer was collected by filtration, washed with methanol, and dried under vacuum for overnight. Compound **1a**: ^{1}H NMR (CDCl$_3$, δ ppm): 6.62 (s, 2H, Ar-**H**), 2.19 (s, Ar-**CH$_3$**). ^{13}C NMR (CDCl$_3$, δ ppm): 16.00, 120.03, 126.06, 150.07.

The similar procedure was used for synthesis of poly(2,5-diisopropyl-1,4-phenylene oxide)s (**1b**), except that for diisopropyl analogue, only 0.032 g manganese catalyst was employed and 0.1 g (0.77 mmol) of dibutylamine, 0.5 g (2.84 mmol) of 2,5-diisopropylphenol, and 0.1 g (1.25 mmol) of 50% NaOH aqueous solution were added, respectively. Compound **1b**: ^{1}H NMR (CDCl$_3$, δ ppm): 6.73 (s, 2H, Ar-**H**), 3.30 (bs, 1H, Ar-**CH**(CCH$_3$)$_2$, 1.15 (bs, 6H, Ar-CH(CC**H$_3$**)$_2$). ^{13}C NMR (CDCl$_3$, δ ppm): 22.96, 26.88, 115.89, 137.20, 150.09.

RESULTS AND DISCUSSION

Preparation and characterization of catalyst

The synthesis of the poly(2,5-dialkyl-1,4-phenylene oxide)s was carried out by oxidative carbon–oxygen coupling reaction of the 2,5-dialkylphenol in toluene using manganese benziloxime and DBA catalyst as shown in Table I. When made basic with sodium hydroxide solution and treated with continuous flow of oxygen through the reaction mixture, the manganese complex was oxidized to higher oxidation states for polymerization reaction. Oximes have been used as chelating ligands for a variety transition metals and displayed rich coordination chemistry and reactivity due to different binding modes.[10–13] The carbonyl oxime ligands such as benziloxime, diacetyl monoxime, and 1,2-naphthoquinone monooxime, however, tend to bind the metal via the nitrogen and carbonyl oxygen sites, forming a five-member metallacyclo ring structure in literatures.[14–16] In this study, α-benzoin oxime was reacted with manganese chloride prior to the initiation of polymerization.

Reaction of MnCl$_2$•4H$_2$O in methanol with α-benzoin oxime in a mole ratio of 2 : 1 yielded the manganese complex wherein the benzoin oxime (C$_6$H$_5$CH(OH)C(=NOH)C$_6$H$_5$) was believed to convert to benzil oxime (C$_6$H$_5$COC(=NOH)C$_6$H$_5$) upon the coordination to the metal center in the presence of oxygen. Structure analogues of such transition metal complexes for cobalt(III), nickel(II), and copper(II) containing one to three benziloxime ligands have been synthesized and characterized recently.[14] The ^{13}C NMR spectrum of manganese benziloxime complex disclosed two typical signals for carbonyl group (—**C**OC$_6$H$_5$) and oxime group (—**C**(C$_6$H$_5$)=N—OH), at δ = 177.72 and 149.51 ppm, respectively, and there appeared no peak between δ = 60 and 80 ppm region assignable to the initial benzoin structure (—**C**H(OH)C$_6$H$_5$). The ^{1}H NMR spectrum
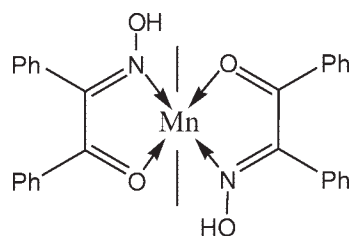
**Figure 1** Proposed coordination mode of manganese benziloxime catalyst.

showed signals for the aromatic protons of benziloxime at $\delta = 7$–8 ppm and exhibited no appearance of the characteristic benzoin proton ($-CH(OH)C_6H_5$) at $\delta = 5.59$ ppm of the free ligand which was consistent with the benzil oxime structure. A concomitant down-field shift of ortho protons due to the deshielding effect from carbonyl group was observed at $\delta = 7.98$ ppm which also revealed the benzil oxime formation as compared to that of other benzoyl type ortho protons such as benzil ($\delta = 7.99$ ppm) or methyl benzoate ($\delta = 8.02$ ppm). Further evidence for coordinated benzil oxime structure was accounted by the FTIR spectrum. The spectrum exhibited a new peak at 1628 cm^{-1} which could be assigned to the $C=O$ stretching of benzil oxime. Other characteristic absorptions such as the $\nu(C=N)$, $\nu_{asy}(C-C_6H_5)$, and the $\nu(N-O)$ frequency were observed at 1596, 1494, and 1223 cm^{-1}, respectively. The N—O stretching vibration in the free α-benzoin oxime ligand appearing at 1195 cm^{-1} was shifted to higher frequencies at 1223 cm^{-1}, indicating the coordination of the oxime group to the metal center. This is in accordance with the results reported by Reddy,[14] wherein the $\nu(N-O)$ was shifted downwards from 1211 to 1269–1277 cm^{-1} when benzil-α-monoxime was coordinated to the nickel, copper, and cobalt center. The spectral results of manganese benziloxime complex are available in the Supporting Information. Accordingly, the benziloxime group is proposed to coordinate to manganese through a bidentate binding mode as depicted in Figure 1.

Preparation and structure analysis of poly(2,5-dialkyl-1,4-phenylene oxide)s

The results of synthesis and analysis of the poly(2,5-dialkyl-1,4-phenylene oxide)s are given in Table I. All polymers **1a** and **1b** were isolated as light brown powders with no detectable tetramethyldiphenoquinone impurities and the structures were characterized by ^1H and ^{13}C NMR. Evidence for regioselectivity was accounted by the ^1H NMR chemical shifts in which the linear linkage through 1,4-C-O coupling was confirmed by two singlets at $\delta = 2.19$ and 6.63 ppm for the symmetrical methyl groups and corresponding aromatic protons; whereas the

nonregioselective product, prepared by conventional CuBr/dibutylamine catalyst, gave two broad humps with chemical shifts ranging over 1 ppm for both methyl and phenyl protons due to the large extent of 1,2-branching [Fig. 2(a)]. Different reaction conditions were attempted to improve the regularity of polymer structure and it was found that the regioselectivity could be enhanced by raising the reaction temperature and concomitantly employing molecular sieves as catalyst support for polymerization reaction conditions. A representative ^1H NMR spectrum of polymer **1** prepared under different reaction conditions is shown in Figure 2. In Figure 2, the sharpening of chemical shifts at 2.19 and 6.63 ppm could be seen clearly when comparing 2b with 2d and 2c with 2e, wherein the increase in temperature led to a significant increment in regioselectivity. On the other hand, the improvement of structure regularity caused by the molecular sieves support, although with less efficiency, could also be noticed by comparing the broadness of ^1H NMR chemical shifts between 2b and 2c as well as 2d and 2e. Thus, the order of regioselectivity could be roughly set as: 90°C/molecular sieves-supported manganese benziloxime catalyst > 90°C/manganese benziloxime catalyst, which is approximately equal to 25°C/molecular sieves-supported manganese benziloxime catalyst > 25°C/manganese benziloxime catalyst.

Further structural verification was confirmed by the ^{13}C NMR spectra which exhibited all the three
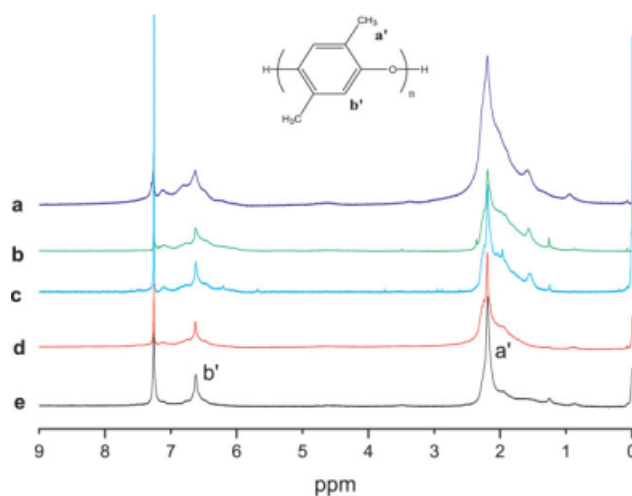
Figure 2 The ^1H NMR spectrum of **1a** preparing under different reaction conditions (a) CuBr/dibutylamine catalyst system at 90°C, (b) manganese benziloxime complex system at 25°C, (c) molecular sieve-supported manganese benziloxime catalyst system at 25°C, (d) manganese benziloxime complex system at 90°C, and (e) molecular sieve-supported manganese benziloxime catalyst system at 90°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
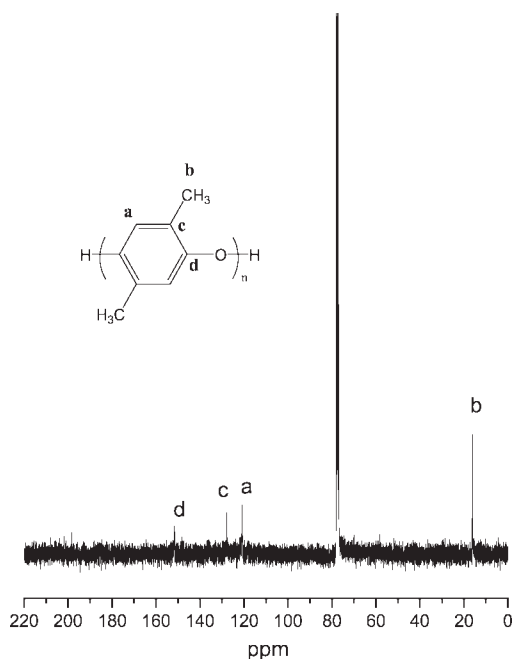
Figure 3 ^{13}C NMR spectra of polymer **1a** in CDCl$_3$ at 25°C.

resonances for aromatic carbon atoms (150.67, 126.97, 120.02) and one for the methyl carbon (15.98) revealing an exclusive 1,4-C-O linkage structure (Fig. 3). Likewise, use of 2,5-diisopropylphenol as monomer under similar conditions provided the corresponding linear polymer wherein the ^{1}H NMR spectrum disclosed three broad signals at δ = 1.16 ppm (Ar-CH(**CH$_3$**)$_2$), 3.31 ppm (Ar-C**H**(CH$_3$)$_2$), and 6.74 ppm (Ar-**H**), respectively, and ^{13}C NMR spectra exhibited all the three resonances for aromatic carbon atoms (150.10, 137.20, 115.89) and two for the isopropyl carbons (26.88, 22.96).

Many articles have been published on the reaction mechanism of oxidative coupling reactions of dialkylphenols and it is generally accepted that phenoxy radicals are involved in chain extension mechanism.[4] Presumably the aryloxy radicals, formed initially by the oxidation of 2,5-dialkylphenols, were coordinated to the manganese benziloxime complex which prevented the ortho positions from attack in certain extent due to the bulkiness of ligands and consequently resulted in the regiocontrolled selectivity at para positions. It is thought that the preclusion effect became more prominent when the manganese catalyst was embedded into the pore system of molecular sieves in which the microenvironment restrict the branch linkage; or/and when oxygen supply became less abundant when the polymerization was conducted at higher reaction temperature. Attempts to carry out the polymerization reaction in the absence of DBA resulted in no product formation under similar reaction conditions.

It is inferred that the mixed-ligand catalyst system (DBA and benziloxime) might have provided enhanced complex stability due to the hindered diamine.[1,17,18]

Thermal properties of poly(2,5-dialkyl-1,4-phenylene oxide)s

The melting behaviors of polymers were examined with differential scanning calorimetry (DSC) and results showed that melting and crystallization of polymer occurred at 327.8 and 306.8°C, respectively, revealing that a highly stereoregular structure with little or no branching existed in polymer matrix. The heat-reversible crystallinity behavior was investigated by heating the samples at a rate of 80°C/min from room temperature to 350°C, held there for 5 min and then cooled to 50°C in fast equilibrium to obtain amorphous state samples, then repeated the program at a rate of 10°C/min for both heating and cooling. The second heating and first cooling process were analyzed for the melting and crystallization points. The DSC traces of the polymer (entry 4) are illustrated in Figure 4. No endothermic peak was observed for **1b** which is probably due to the less regular packing of the bulky side groups attached to polymer chains. The crystallinity was also estimated by WAXS and the scattering pattern which showed strong peaks at 2θ values of 15.81°, 17.02°, 18.81°, 19.96°, 24.39°, 28.18° as illustrated in Figure 5. The phase relationships was analyzed by XRD pattern processing software Jade 5.0 and the degree of crystallinity was calculated approximately 23.7%.

Thermal stabilities of polymers were examined by thermogravimetric analysis (TGA) with the 5 wt % decomposition temperature ($T_{d,5\%}$) and the results are given in Table I. Polymers **1a** generally displayed higher $T_{d,5\%}$ and char yield than the **1b** analogues
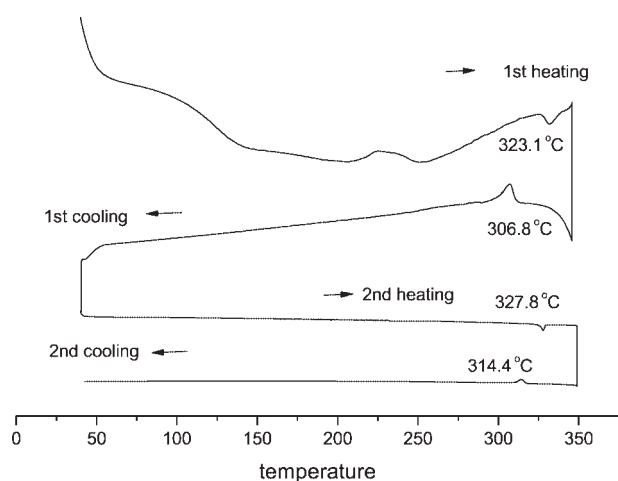
Figure 4 DSC scans of the poly(2,5-dimethyl-1,4-phenylene oxide)s.
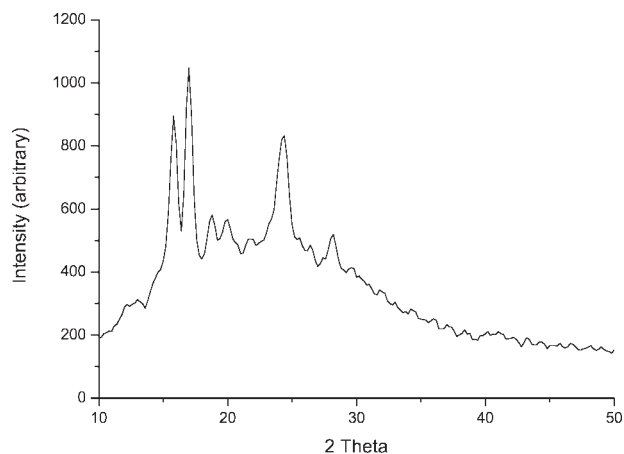
Figure 5 Wide-angle X-ray scattering (WAXS) of poly(2,5-dimethyl-1,4-phenylene oxide)s.

indicating that the conformational disorder introduced by isopropyl group may have enhanced the thermal degradation of polymer and reduced its thermal stability. Moreover, the increment of crystallinity might be explained for the higher $T_{d,5\%}$ values for entry 4 versus entry 1, 2, and 3. Typical TGA thermograms of **1a** and **1b** polymers are shown in Figure 6.

Although the polymers prepared at higher temperature conditions generally displayed a lower polydispersity than other polymers, their average molecular weights M_n and M_w were also lower as analyzed by GPC. The molecular weights obtained at ambient temperature (entry 1, 3, and 5) were generally higher than those at 90°C, (entry 2, 4, 6, and 7) accompanied with more branching or crosslinking at ortho positions. It was inferred that the exothermic C-O coupling reaction would generally be favored by higher oxygen solubility at ambient temperature and afforded more random linkages with higher molecular weights. Similar trend was also noted for the conventional PPO polymerization reaction. Appreciable amount of polymers ($\sim 12\%$) was found to adsorb on molecular sieves, which could be recovered by extracting the molecular sieves-supported catalysts with chloroform followed by precipitating into a 15-fold excess of stirred methanol. This result might explain the loss of yields of entry 4 and 7 comparing to other entries when the reactions were conducted on the molecular sieves. Another decrement of yields resulted from the product solubility in decant solutions during the course of purifications. Decanting and removal of solvent left a small amount of brown residue yielding about 18% of crude polymer with lower molecular weights and small amount of unknown impurities.

Compared to the conventional poly(2,6-dimethyl-1,4-phenylene oxide)s, the low molecular weights and relatively low yields of polymers **1a** and **1b**

could also be due to the higher oxidation potential of 2,5-dialkylphenols which made the polymerization proceed less favorably and might have deferred the C-O coupling.[19] The oxidation potentials for 2,5-DMP, 2,5-DIPP, and 2,6-DMP were measured as 0.429, 0.426, and 0.407 V, respectively, based on cyclic voltammograms. Moreover, the poor solubility of the poly(2,5-dialkyl-1,4-phenylene oxide)s in toluene resulted in early precipitation of polymer which seemed unlikely for polymers **1a** and **1b** to achieve high molecular weight under the reaction conditions.

CONCLUSIONS

Considerable interest has been developed on the synthesis of high performance polymers owing to the increasing demand of new materials for the electronic and chemical industry.[20] In this work, we developed a facial method to control the regioselectivity of oxidative polymerization of poly(2,5-dialkyl-1,4-phenylene oxide)s under mild reaction conditions and the resulting polymers possessed a melting point higher than the poly(p-phenylene sulfide) (PPS, $T_m = 290$°C) or type II liquid crystalline polymer. The manganese benziloxime and DBA catalyst exhibited an improved 1, 4-C-O coupling selectivity by raising the reaction temperature and concomitantly employing molecular sieves as catalyst support for polymerization reaction. The poly(2,5-dimethyl-1,4-phenylene oxide)s exhibited heat-reversible crystalline behavior with melting and crystallization during DSC measurements which might lead to the applications of new melt-molding materials for better thermal and solvent resistance properties.
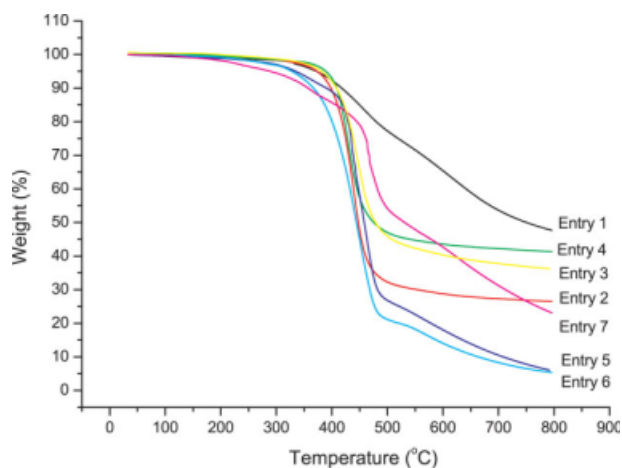
Figure 6 TGA thermograms of poly(2,5-dimethyl-1,4-phenylene oxide)s under nitrogen. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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