Synthesis of poly(2,6-dimethyl-1,4-phenylene oxide) by oxidative coupling

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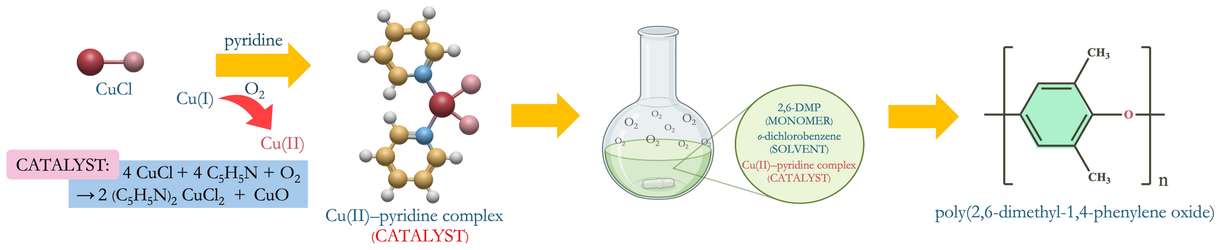
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ABSTRACT

In this research project, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was synthesized via the oxidative coupling using a Cu(II)-amine catalytic system under oxygen atmosphere in order to study various factors affecting the reaction rate. The factors investigated included different isomer of dimethylphenol monomers, stirrer speed, type of amines, catalyst concentrations and temperatures. The results showed that substitution of dimethyl on the phenolic ring has profound affected on the reaction rate. At room temperature, 2,6-dimethylphenol provided the highest reaction rate of 3.3×10^{-3} M·min^{-1}. Viscosity-average molecular weight ($\overline{M}_v$) showed 1.62×10^5 and 90% yield was obtained. In contrast, other isomers exhibited obviously slower reaction rates and lower molecular weights. Increasing both stirrer speed and catalyst concentration significantly enhanced the reaction rate as expected since this oxidative coupling is zero-order kinetic reaction. In addition, monodentate amine ligands facilitated the formation of a Cu(II)-amine complex suitable for catalysis at ambient temperature. ^{1}H-NMR and ATR-FTIR confirmed that this synthesized polymer corresponded to poly(2,6-dimethyl-1,4-phenylene oxide). DSC analysis revealed high melting point in range of 205-235 °C, which is consistent with the thermal properties of PPO and very useful in a high-performance engineering thermoplastic applications. These results demonstrate the various factors affecting the reaction rate and provide guidance for determining optimal conditions for the synthesis of poly(2,6-dimethyl-1,4-phenylene oxide).

INTRODUCTION

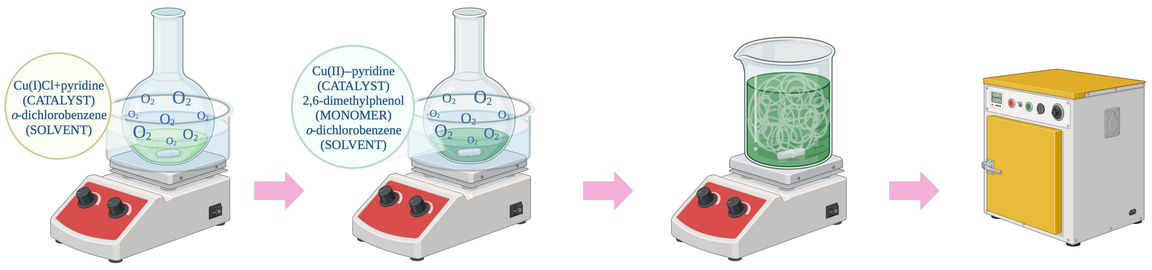
Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was first synthesized by Allan S. Hay in 1956. It is widely used in engineering plastic applications due to its excellent thermal resistance and electrical insulating properties. This polymer can be synthesized via environmentally friendly oxidative coupling polymerization at ambient temperature. For application used, it is often blended with polystyrene and other additives and marketed under the trade name Noryl® resin.



RESEARCH OBJECTIVES

- To synthesis poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and to characterized the obtained polymers.
- To investigate the effects of various factors on the reaction rate of PPO synthesis including isomer of dimethylphenol monomers, stirrer speed, type of amines, catalyst concentrations and temperatures.

METHODOLOGY



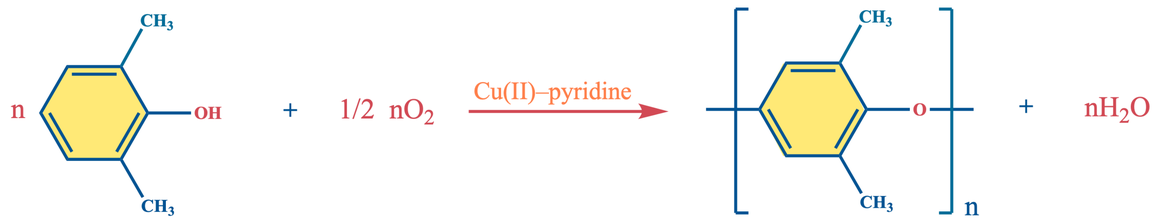
Stir the catalyst for 30 minutes light green to dark green (Cu(II)–pyridine complex)

2,6-dimethylphenol monomer solution to run quickly into the reaction flask with continued stirring.

Polymer was precipitated in methanol containing conc.HCl, then dissolved in chloroform and reprecipitate for final purification.

Filter the polymer by suction through a sintered glass filter, then dry in a vacuum oven at 60 °C to constant weight.

CHEMICAL REACTION



2,6-dimethylphenol (2,6-DMP)

poly(2,6-dimethyl-1,4-phenylene oxide)

RESULTS AND DISCUSSSION

FACTORS AFFECT REACTION RATE

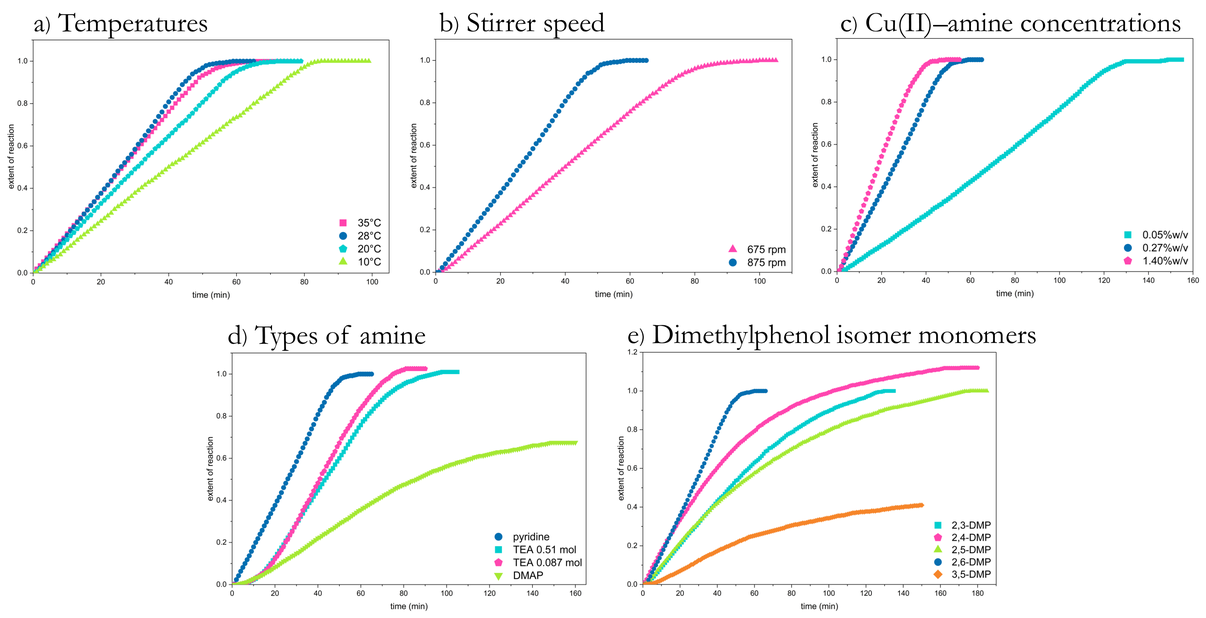


Fig. 1 Zero-order graph of extent of reaction against time; a) temperatures, b) stirrer speed, c) Cu(II)–amine concentrations, d) types of amine and e) isomer of dimethylphenol (DMP) monomer.

VISCOSITY-AVERAGE MOLECULAR WEIGHT ($\overline{M}_v$)

Table 1 Effects of reaction conditions on the viscosity-average molecular weight of poly(2,6-dimethyl-1,4-phenylene oxide)

Run	Temperature (°C)	Stirrer speed (rpm)	Cu(I)Cl concentration (%w/v)	[η] (dL·g^{-1})	$\overline{M}_v$
1	28	875	0.27	1.044	1.62×10^5
2	35	875	0.27	0.502	5.18×10^4
3	20	875	0.27	0.618	7.16×10^4
4	10	875	0.27	0.570	6.31×10^4
5	28	675	0.27	0.736	9.40×10^4
6	28	875	1.40	0.657	7.88×10^4
7	28	875	0.05	0.634	7.45×10^4

Poly(2,6-dimethyl-1,4-phenylene oxide) synthesized at room temperature under high stirrer speed and with an optimal amount of Cu(II)–amine exhibited a significant increase in viscosity-average molecular weight, producing a long-chain polymer with an $\overline{M}_v$ of up to 1.62×10^5 g·mol^{-1}.

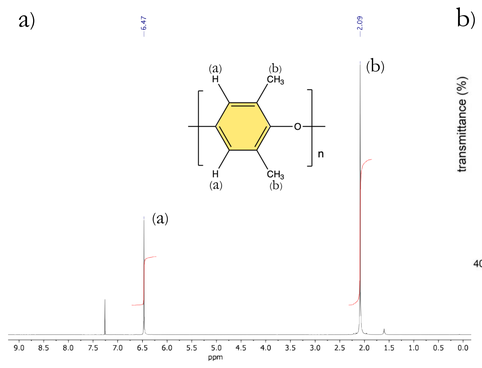
REACTION RATE AND PRODUCT YIELD

Table 2 Percent yield and zero-order rate constant (k)

Run	Temperature (°C)	Stirrer speed (rpm)	Cu(I)Cl concentration (%w/v)	Type of amine	Isomers of DMP	%Yield	Rate constant (M min^{-1})
1	28	875	0.27	pyridine	2,6-DMP	90	3.3×10^{-3}
2	35	875	0.27	pyridine	2,6-DMP	84	3.1×10^{-3}
3	20	875	0.27	pyridine	2,6-DMP	86	2.6×10^{-3}
4	10	875	0.27	pyridine	2,6-DMP	86	2.0×10^{-3}
5	28	675	0.27	pyridine	2,6-DMP	86	2.1×10^{-3}
6	28	875	1.40	pyridine	2,6-DMP	87	4.4×10^{-3}
7	28	875	0.05	pyridine	2,6-DMP	86	1.2×10^{-3}
8	28	875	0.27	TEA	2,6-DMP	58	3.0×10^{-3}
9	28	875	0.27	DMAP	2,6-DMP	3	1.1×10^{-3}
10	28	875	0.27	pyridine	2,3-DMP	9	1.8×10^{-3}
11	28	875	0.27	pyridine	2,4-DMP	-	2.7×10^{-3}
12	28	875	0.27	pyridine	2,5-DMP	5	1.9×10^{-3}
13	28	875	0.27	pyridine	3,5-DMP	-	7.7×10^{-4}

Under the optimal conditions for poly(2,6-dimethyl-1,4-phenylene oxideX synthesis, the reaction rate was 3.3×10^{-3} M·min^{-1} and the percent yield reached approximately 90%. These conditions involved the use of 2,6-dimethylphenol at high stirrer speed and room temperature, with a Cu(II)–pyridine complex catalyst.

CHARACTERIZATIONS



Proton chemical shift (ppm)	Assignment
2.09	Methyl proton (-CH_3) (a)
6.47	Proton of benzene ring (b)

Vibrational assignment	Wavenumber (cm^{-1})
C–H stretching (Aromatic ring)	3030
C–H stretching (Methyl group)	2950–2850
C=C stretching (Aromatic ring)	1600–1450
C–O stretching (Ar–O–Ar (ether))	1200
C–H out-of-plane bending (Para-disubstituted)	830

- ^{1}H-NMR analysis revealed an integral ratio (a:b) of approximately 1:3, which is consistent with the repeating unit of PPO.
- FTIR spectra confirmed characteristic absorption bands of a para-substituted benzene ring and functional groups of PPO.

Fig. 2 Characterization of poly(2,6-dimethyl-1,4-phenylene oxide) using; a)^{1}H-NMR and b) ATR-FTIR techniques.

CONCLUSIONS

- Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was successfully synthesized with approximately 90% yield. The polymer structure was confirmed by ^{1}H-NMR and FTIR analysis.
- The reaction proceeded rapidly at room temperature; high stirrer speed and Cu(II)–amine catalyst concentration significantly affected the reaction rate.
- The type of amine influenced the formation of a stable catalyst complex, while the substitution position of the dimethylphenol isomer significantly affected the reaction kinetics.
- The optimal conditions for oxidative coupling involved 2,6-dimethylphenol and a Cu(II)–pyridine catalyst at room temperature.

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