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OXIDATIVE POLYMERIZATION OF 2,6-DIMETHYLPHENOL BY COPPER(II)CHLORIDE-AMINE COMPLEXES: EFFECT OF AMINES ON POLYMERIZATION ACTIVITY.*

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ABSTRACT

2,6-Dimethylphenol (2,6-DMP) undergoes oxidative polymerization with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ -aliphatic amine complexes in a 70:30(v/v) o-dichlorobenzene-ethanol solvent. Unlike pyridine, polymerization occurs even in the absence of added base. Apart from basicity, factors such as steric effects and nature of ligand coordination to Cu(II) have profound effect on catalyst reactivity.

INTRODUCTION

Since the discovery of oxidative polymerization of 2,6-dimethylphenol (2,6-DMP) by copper(I)chloride- O_2 -pyridine complex by Hay and coworkers (1) a variety of copper-amine complex systems have been reported as catalysts in both published and patented literature (2,3). In spite of the extensive literature on such catalysts, few studies are available on the effect of amine structure on catalyst efficiency. With the Cu(I)Cl-pyridine system, steric factors were found to affect both the rate and selectivity of oxidative coupling, using a series of pyridines substituted in the 2- and 6-position (4). From a more detailed kinetic analysis Tsuchida and coworkers concluded that with Cu(I)Cl-amine systems, the difference in the activities

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of amine ligands in the region of low monomer concentrations are related to both the ease of electron transfer as well as steric bulk of the ligand (5). Pyridine was found to be more effective than aliphatic amines as evidenced by a large value of equilibrium constant associated with the formation of the intermediate complex ES in the well known Michaelis-Menten equation. On the contrary, Cu(II)Cl_2 -pyridine is inactive as a catalyst for oxidative polymerization, because, for electron transfer between $\text{Cu(II)}/2,6\text{-DMP}$, a ligand complex of low coordination is believed to be necessary (6). Surprisingly oxidative polymerization with Cu(II)Cl_2 -aliphatic amines have not been reported in the literature. We therefore undertook a systematic study on the effect of various aliphatic amines on the oxidative polymerization of 2,6-DMP using copper(II)chloride dihydrate as catalyst. This paper reports the results of this study.

EXPERIMENTAL

Materials: Commercial 2,6-DMP was recrystallized from n-hexane and dried under vacuum prior to use. Reagent grade $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was used as received. The various amines were purified prior to use by standard procedures. O-dichlorobenzene was fractionally distilled and a constant boiling middle fraction was used for reaction. Ethanol was distilled prior to use.

Oxidation Procedure: The oxidative polymerization was run in a 250 mL three necked cylindrical flask provided with a jacket, magnetic stirrer and a thermometer. One of the outlet was connected to a gas burette and a U-tube manometer. The third outlet capped with a self sealing rubber septum, was used for charging the monomer. In a typical experiment, the desired quantities of o-dichlorobenzene-ethanol (70:30 v/v), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and an amine was charged to the reaction flask. After dissolution of the catalyst components, oxygen was purged through the flask for 20-30 minutes at $30 \pm 0.1^\circ\text{C}$. Oxygen saturation led to catalyst complex formation indicated by change of green Cu(II) color to either blue or orange depending on the nature of amine. At this point 20 mL of a 0.2M solution of 2,6-DMP in o-dichlorobenzene-ethanol was slowly introduced into the flask by means of a hypodermic syringe. Oxygen uptake started without any induction period and was recorded as a function of time. The reaction mixture turned wine red. Depending on the amine used, the polymer precipitated at varying time intervals. The reaction was continued till oxygen absorption ceased. Thereafter the mixture was poured in methanol containing 5 vol% conc.

HCl, washed, filtered and dried. In all experiments, less than 0.1% by weight of 3,3',5,5'-tetramethyl-4,4'-diphenylquinone (DPQ) was detected (7).

The reaction rate, R_{\max} , was calculated from the maximum slope of the oxygen consumption curve. Intrinsic viscosity was measured in an Ubbelohde dilution viscometer in chloroform at $30 \pm 0.1^\circ\text{C}$.

RESULTS AND DISCUSSION

The oxidative polymerization of 2,6-DMP with copper (II)chloride dihydrate and various amines was performed in *o*-dichlorobenzene-ethanol (70:30 v/v) at $30 \pm 0.1^\circ\text{C}$. Most of the earlier studies on oxidative polymerization have been conducted in solvents wherein the polymer has good solubility (example, chloroform, benzene, toluene, *o*-dichlorobenzene etc.). However, patent literature reveals that polymerization can be conducted in solvents where the polymer formed is not completely soluble (8).

The amines used in the study were as follows: secondary amines such as di-*n*-butylamine (acyclic), piperidine and piperazine (cyclic), tertiary amines such as triethylamine and 1,4-diazabicyclo(2.2.2.)octane (DABCO) and 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) and secondary/tertiary amines bearing oxygen functionality such as diethanolamine, triethanolamine and morpholine. The amines spanned a range of pK_a values as well as steric structures.

The nitrogen to copper ligand ratio was varied between 25-100. In this range, the final oxygen absorption uniformly exceeded 100%. The results are shown in Table. The oxygen absorption rate for the various amines at N/Cu ratio of 50 is shown in Figure.

The yield of methanol insoluble polymers are based on dry weights of the isolated product and the weight of 2,6-DMP originally present. The total yield is less than quantitative. This is believed to be due to loss of methanol soluble low molecular weight polymer fractions in the work up. This was confirmed in the case of piperazine where the methanol soluble fractions were predominantly oligomeric poly(phenylene ethers) ($M_n = 475$).

The polymer conversion was invariant with N/Cu ratio. However, the reaction rate showed a pronounced tendency to accelerate at higher N/Cu ratios. In view of the high ligand ratios used and the fact that the final

TABLE
Oxidative Polymerization of 2,6-Dimethylphenol with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ /amine Complex^a

Sr. No.	Amine	pKa	N/Cu	$R_{\text{max}} \times 10^3$ mol/lit/min.	Polymer yield, %	Heterogeneity time, min	$[\eta]$, dl/g ^b
1.	Di-n-butylamine	11.2	25	6.3	93	35	0.47
			50	8.0	94	40	0.46
			75	8.5	93	36	0.43
2.	Piperidine	11.2	100	10.2	92	26	0.45
			25	8.2	88	24	0.92
			50	28.2	90	10	0.68
			75	21.6	89	13	0.65
			100	22.0	89	13	0.52
3.	Piperazine	9.8	50	4.7	12	c	0.19
			25	0.75	86	300	0.53
4.	Triethylamine	10.7	50	0.64	86	300	0.52
			75	1.00	74	210	0.57
			100	0.97	89	200	0.61
5.	DBU	11.5	50	6.0	32	c	0.14
			25	11.6	90	30	0.82
6.	Morpholine	8.4	50	12.0	86	20	0.90
			75	12.8	91	18	0.98
			100	13.0	87	14	0.93

^a 2,6-DMP: 0.20 M, Amine: 0.125-0.50 M, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$: 0.005 M, o-dichlorobenzene-ethanol (70:30 v/v): 100 mL, Temperature 30 ± 0.1 °C.

^b In CHCl_3 at 30 ± 0.1 °C.

^c No heterogeneity appeared till the end of the reaction.

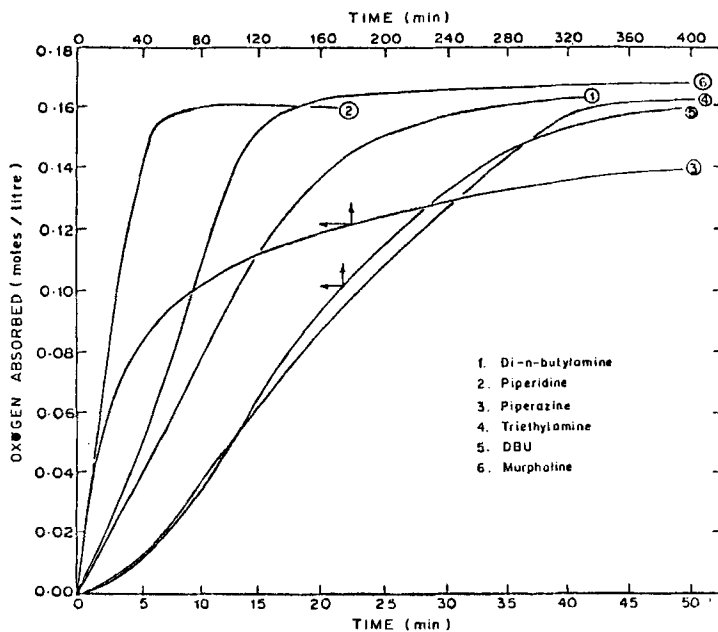
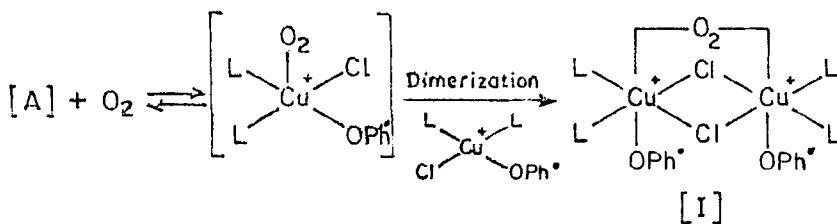
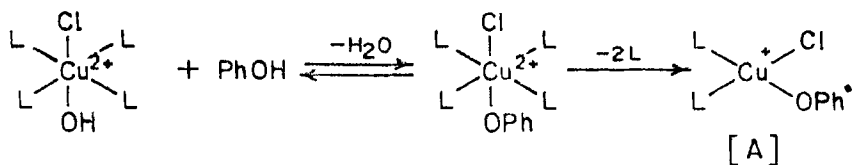


FIG. OXYGEN ABSORPTION VS TIME DURING 2,6-DMP POLYMERIZATION WITH VARIOUS AMINES AT 50 AMINE TO COPPER MOLAR RATIO



SCHEME

oxygen consumption uniformly exceeds 100%, it was concluded that the autoretardation effect due to water formed in the reaction was not important. In all cases, selectivity to C-O coupling product was greater than 99%. The intrinsic viscosity of the polymer decreased in the order, (N/Cu = 50), morpholine > piperidine > di-n-butylamine >> piperazine \approx DBU.

Of the amines studied, DABCO, diethanolamine and triethanolamine showed no oxygen uptake. For the four secondary amines examined, the polymerization rate (R_{\max} at N/Cu=50) decreased in the order piperidine > morpholine > di-n-butylamine > piperazine. These observations establish that pKa of bases alone do not determine catalyst activity.

Oxidative polymerization of 2,6-DMP with Cu(II)-amine complexes is believed to involve the intermediacy of a six coordinated octahedral complex, wherein the amine occupies the four square planar coordination spheres and a rate determining dimerization step resulting in the formation of a binuclear complex(I)(Scheme) (9).

A sterically demanding amine such as di-n-butylamine may be expected to react slowly compared to piperidine. For the same reason triethylamine also showed diminished activity. DABCO, a less sterically hindered nitrogen base, did not also show any polymerization activity. This could be due to its relatively weak basicity in hydroxylic medium. Of the three oxygen containing bases of almost similar pKa's only morpholine showed good polymerization activity in conjunction with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Diethanolamine and triethanolamine are bidentate ligands capable of coordination to copper(II) through both nitrogen and oxygen (10). This may inhibit electron transfer between Cu(II)/2,6-DMP which is favored by a complex of low coordination (6). Morpholine is a monodentate ligand capable of coordination only through nitrogen and hence is active. The lower pKa of morpholine relative to piperidine results in reduced catalyst activity.

Surprisingly, piperazine showed very poor activity even though it has a structure similar to morpholine. Also, N,N'-di-tert-butylethylenediamine has a structure similar to piperazine with a relatively more hindered environment around nitrogen is reported to be an active catalyst in conjunction with Cu(II) (11). Our results suggest that piperazine functions as a weak monodentate ligand to Cu(II) and is even less effective than di-n-butylamine. The reasons for poor conversion is not clear at the present time.

In conclusion, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ forms active oxidative polymerization catalyst with secondary aliphatic amines. Tertiary amines are inactive. Unlike CuCl_2 -pyridine which is active only in presence of an added base like potassium hydroxide (12) aliphatic amine form active catalyst complexes under neutral conditions.

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