

In Situ Preparation of *N,N*-Dimethyl-*n*-butylamine for 2,6-Dimethylphenol Polymerization

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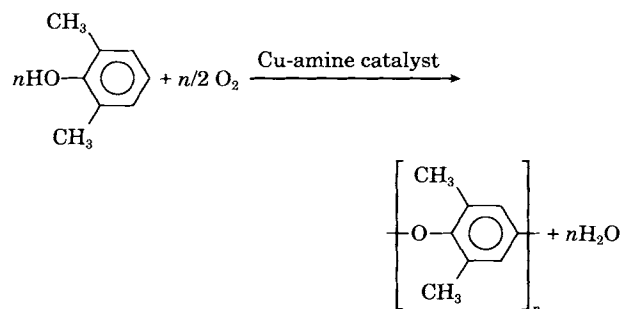
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SYNOPSIS

2,6-Dimethylphenol (2,6-DMP) polymerization with a catalytic complex of $\text{Cu}_2\text{O}/\text{HBr}/N,N'$ -di-*tert*-butylethylene diamine (DBEDA)/*N,N*-dimethyl-*n*-butylamine (DMBA)/dibutylamine (DBA) was studied, in which DMBA was prepared *in situ* from the methylation of *n*-butylamine over four different solid acid catalysts (two different γ -alumina, one silica-alumina, and one zeolite). The effectiveness of the unpurified methylation product solutions for promoting the 2,6-DMP polymerization was strongly dependent on the type of solid acid catalysts used. The performance of the best one (untreated product solution from the methylation reactor with Condea γ -alumina catalyst) was very similar to that of the reagent grade DMBA. Infrared spectrum studies showed that DMBA acted as the external base for the 2,6-DMP polymerization catalyst system to neutralize the excess hydrobromic acid and to increase the polymerization rate. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polyphenylene oxide (PPO) is one of "big five" engineering thermoplastics. The annual sales value of the PPO-based polymer blends exceeds one billion U.S. dollars. PPO is synthesized by the copper-catalyzed oxidative polymerization of 2,6-dimethylphenol (2,6-DMP)¹ according to the following reaction scheme:



Amines such as pyridines, dibutylamine, *n*-butylamine, and aliphatic diamine have been used as the ligands to promote the catalyst activity.² Com-

mercially, PPO is produced using a catalyst system containing cuprous oxide/hydrobromic acid/*N,N'*-di-*tert*-butylethylene diamine (DBEDA)/*N,N*-dimethyl-*n*-butylamine (DMBA)/dibutylamine (DBA). The catalyst system exhibits extremely high activity for the polymerization of 2,6-DMP to PPO.^{3,4} The kinetics and factors affecting the catalyst system have been studied.^{5,6}

Among the three amines used in the $\text{Cu}_2\text{O}/\text{HBr}/\text{DBEDA}/\text{DMBA}/\text{DBA}$ catalyst system, DMBA (a tertiary amine) is the highest in both amount and price (in a typical catalyst formulation for 2,6-DMP polymerization, the amine/copper molar ratio is approximately two for DBEDA, is in the range from 20 to 60 for DMBA, and is approximately 10 for DBA; based on the Tokyo Kasei Organic Chemicals 1992 Catalog, the price of the reagent grade DMBA was 50500 yens/500 mL, and the price of the reagent grade DBA was 2000 yens/500 mL). A traditional approach to synthesize DMBA is by the reaction of *n*-butylamine with formaldehyde in the presence of formic acid.⁷ Tedious separation procedures are needed to remove formic acid and to purify the product. Recently, we developed an approach to produce DMBA by the methylation of *n*-butylamine in the presence of several different solid-acid catalysts.⁸ To save the purification cost for DMBA and

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to improve the PPO process economics, we tried to use the product solutions from the methylation reactor directly for 2,6-DMP polymerization without any purification treatment, and surprisingly found that the performance of one of the unpurified methylation product solutions was very similar to that of the reagent grade DMBA. The polymerization results of using the unpurified methylation product solutions for 2,6-DMP polymerization are reported in this paper.

Although the copper/DBEDA/DMBA catalyst system is used commercially for PPO production, there is no information about the role of DMBA in the polymerization catalyst system. Another purpose of this paper is to study the function of DMBA in the 2,6-DMP polymerization catalyst system to have a better understanding of the important polymerization catalyst system.

EXPERIMENTAL

Methylation of *n*-Butylamine

The reaction of *n*-butylamine and methanol to form *N,N*-dimethyl-*n*-butylamine was performed in a pressurized (gauge pressure = 4 kg/cm²) stainless-steel reactor. Liquid solution with *n*-butylamine and methanol in a 1 : 3 molar ratio was fed to the reactor containing solid acid catalysts where the methylation reaction occurred on the catalyst surface. Four different solid acid catalysts, including a γ -alumina (Na content = 0.15 wt %) from Condea Chemie (Germany), H-152 γ -alumina (Na content = 4 wt %) from Alcoa Chemicals Co. (Pittsburgh, PA, USA), a silica-alumina (SiO₂:Al₂O₃ = 30 : 70) from Condea, and a rare earth ion-exchanged Y zeolite (REY) (65 wt % SiO₂, 22.7 wt % Al₂O₃, 1.6 wt % Na₂O, and 10.7 wt % Re₂O₃) from Strem Chemicals Co. (Newburyport MA, USA), were used to catalyze the reaction between *n*-butylamine and methanol. The methylation product solutions were collected in glass bottles for further use and their compositions were analyzed by a Perkin-Elmer 8410 gas chromatograph equipped with an SP 2100 column and a flame ionization detector. Detailed descriptions about the synthesis of DMBA are given elsewhere.⁸

Polymerization of 2,6-DMP

The oxidative polymerization of 2,6-DMP to PPO was carried out in a 1-L glass reactor equipped with a gas sparger and an agitator. The reactor was immersed in

a constant temperature water bath and both the reactor temperature and the water bath temperature were recorded. The 2,6-DMP was a purified pilot plant product⁹ and had a purity of 99.94% w/w. The copper-amine polymerization catalyst system was prepared by mixing the methylation product solution prepared above with Cu₂O/HBr solution, DBEDA, DBA, and surfactant (trioctylmethylammonium chloride). Unless stated otherwise, the polymerization catalyst had the molar ratios of DMP/DBEDA/DMBA/DBA/surfactant/Br/Cu = 850/1.8/30/8/0.5/5/1. The polymerization catalyst solution was then added to the glass reactor containing 656 g of 15 wt % 2,6-DMP in toluene.

Polymerization was initiated by bubbling pure oxygen (0.5 L/min) through the liquid solution. The inlet and exit gas flow rates were measured with a wet gas meter (Shinagawa Seiki, Tokyo). Unless specified otherwise, the reactor temperature was kept at 25°C and the reaction time was 2 h. At the end of polymerization, 100 mL of 2 wt % EDTA aqueous solution was added into the reactor to stop the reaction. The polymer produced was precipitated with methanol, filtered, washed with methanol, and then dried. Intrinsic viscosity of the dried polymer was measured by a Schoff AVS 300 system at 30°C with chloroform as the solvent.

FTIR Measurements

To study the role of DMBA in the copper-based polymerization catalyst, infrared spectra (KBr disks) of the dried solid samples of DBEDA, Cu/Br/DBEDA complex, and Cu/Br/DBEDA/DMBA were obtained with a Nicolet 510P infrared spectrometer. The Cu/Br/DBEDA complex was prepared by mixing a cuprous oxide/HBr solution (Br/Cu molar ratio = 5) with DBEDA (DBEDA/Cu molar ratio = 2) and the complex formed was washed twice with ethyl ether and then vacuum dried at room temperature. The Cu/Br/DBEDA/DMBA sample was prepared by dissolving part of the dried Cu/Br/DBEDA complex (purple color) prepared above in a reagent grade DMBA solution (DMBA/Cu molar ratio = 60) and the solution (blue color) was vacuum dried at room temperature to obtain a dried solid sample of Cu/Br/DBEDA/DMBA (purple color).

RESULTS AND DISCUSSION

Effect of Methylation Catalysts

Methylation product solutions from four different methylation catalysts were used directly for 2,6-

DMP polymerization without further purification; the results are shown in Table I. Among the four methylation catalysts studied, REY has the highest selectivity (97%) for the reaction between *n*-butylamine and methanol to DMBA, however, the unpurified methylation product solution from REY has the lowest promotion effectiveness for the 2,6-DMP polymerization, which resulted in the lowest PPO molecular weight (PPO I.V. was 0.07 dL/g for 1 h reaction time and was 0.11 dL/g for 2 h reaction time). For the other three methylation catalysts, the methylation product solution with higher DMBA selectivity acted as the better promoter for the copper-based polymerization catalyst (i.e., produced PPO with higher intrinsic viscosity). Among the four methylation catalysts studied, the performance of the unpurified product solution from Condea γ -alumina (produced PPO with I.V. = 0.56 dL/g for 1 h reaction time, and I.V. = 0.63 dL/g for 2 h reaction time) was superior to others.

The reason for the unusually low promotion effectiveness of the unpurified methylation product solution from the REY catalyst may be because it contains some impurities which are poisonous to the copper-based polymerization catalyst. To remove the poisonous materials, we extracted the product solution from REY with an equal amount of toluene and repeated the polymerization experiment. After the extraction procedure, the intrinsic viscosity of PPO produced increased from 0.11 to 0.553 dL/g for 2 h reaction time, as shown in Table I. The result suggests that most of the poisonous material in the untreated methylation solution from REY can be removed by the extraction process.

Among the four methylation catalysts studied, the methylation product solution from Condea γ -alumina had the best performance for 2,6-DMP polymerization, therefore, it was used for the following studies.

Effect of DMBA Sources

Three different sources of DMBA were used for 2,6-DMP polymerization (source A: unpurified methylation product solution directly from the methylation reactor catalyzed by Condea γ -alumina; source B: the solution obtained by extracting source A solution with equal weight of toluene; source C: reagent grade DMBA with purity > 99% which was purchased from Tokyo Kasei Kaygo Co., Japan). Polymer with I.V. = 0.63 dL/g was obtained by using the unpurified product mixture of *n*-butylamine methylation (source A, DMBA/Cu = 30), which was approximately the same as the polymer obtained

(I.V. = 0.67 dL/g) using the same weight of reagent grade DMBA (source C, DMBA/Cu = 60). The result suggests that effectiveness of the untreated methylation product solution (from Condea γ -alumina) for promoting 2,6-DMP polymerization is approximately the same as that of reagent grade DMBA.

For source B, the methylation product solution from Condea γ -alumina was extracted with an equal weight of toluene to obtain an 85 wt % organic layer and 15 wt % aqueous layer (water was produced from the reaction between *n*-butylamine and methanol). The distribution coefficient of DMBA (concentration of DMBA in organic phase/concentration of DMBA in aqueous phase) was found to be 19.4 and about 1 wt % of DMBA was lost in the aqueous phase. The aqueous phase also contained a large portion of the unreacted methanol. The organic phase was used to prepare the polymerization catalyst (DMBA/Cu molar ratio = 30) and the PPO I.V. obtained was 0.63 dL/g, which was identical to that obtained by using the unpurified methylation product solution (source A). The result suggests that the copper-based polymerization catalyst activity is not affected by the presence of water and other side products (GC-MS analysis indicated that *N*-butyl ether, *N*-butyl-*N*-methyl-1-butaneamine, *N,N,N',N'*-tetrabutylmethanediamine, and 1-methylpiperazine were the major by-products) from the methylation of *n*-butylamine on the Condea γ -alumina.

Effect of *n*-Butylamine Conversion

The effect of *n*-butylamine conversion on the performance of the unpurified methylation product solution was studied by using two different *n*-butylamine conversion (37 and 100%). At 37% *n*-butylamine conversion, the major product was *N*-methyl-*n*-butylamine and therefore the selectivity of DMBA (= 35%) was much less than that at 100% *n*-butylamine conversion, which had 88.7% DMBA selectivity. PPO produced with the former had an I.V. value of 0.48 dL/g, which was less than that produced with the latter (PPO I.V. = 0.63 dL/g). But the PPO produced with the former still had enough I.V. value for commercial application (commercial PPO usually has I.V. values between 0.4 and 0.5 dL/g).

Effect of DMBA Amount

Figure 1 shows the change of PPO I.V. as a function of the DMBA/Cu ratio by using the unpurified methylation product solution. The intrinsic viscosity

Table I Effect of Methylation Catalyst on the Performances of Unpurified Methylation Product Solutions for PPO Polymerization^a

Methylation Catalyst	Condea γ -Alumina	Alcoa H-152	Silica-Alumina	REY	REY (Extracted)
DMBA selectivity	88.7%	60%	56%	97%	
PPO I.V. (dL/g)	0.56 (1 h) 0.63 (2 h)	0.41 (1 h)	0.10 (1 h) 0.13 (2 h)	0.07 (1 h) 0.11 (2 h)	0.37 (1 h) 0.55 (2 h)

^a Reaction temperature = 25°C.

values of PPO decreased with the decrease of DMBA/Cu ratio. The tendency of the change was slow at higher DMBA/Cu ratio (for example, PPO I.V. values only changed from 0.63 to 0.58 dL/g as DMBA/Cu ratios decreased from 32 to 16), which means that the polymerization catalyst activity is insensitive to the change of DMBA/Cu ratio in this range. The tendency of the change of PPO I.V. was rapid at lower DMBA/Cu ratio (PPO I.V. values changed from 0.58 dL/g to 0 as DMBA/Cu ratios changed from 16 to 0), which suggests that the polymerization catalyst activity is much more sensitive to the DMBA/Cu change at a lower DMBA/Cu molar ratio. The results also suggest that a large excess of DMBA is not required to obtain high-molecular-weight polymer and a DMBA/Cu molar ratio of eight is sufficient to produce PPO with commercial acceptable molecular weight.

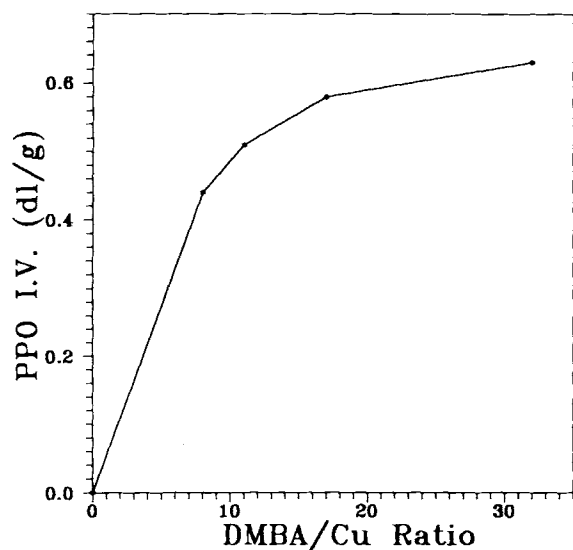
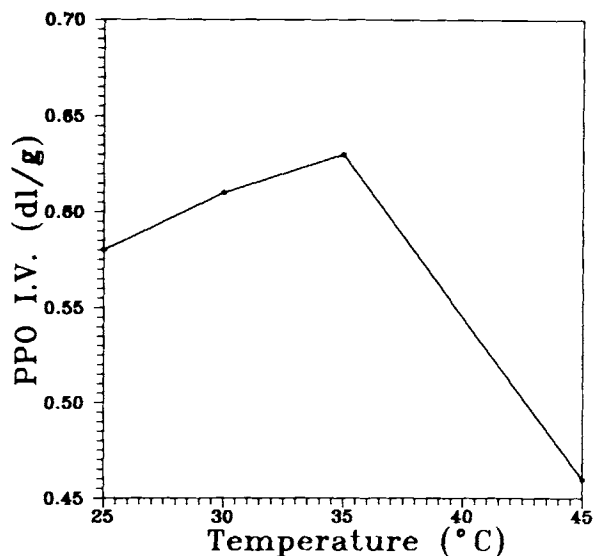
Effect of Reaction Temperature

Figure 2 shows the effect of reaction temperature on PPO I.V. obtained by using the unpurified meth-

ylation product solution from Condea γ -alumina. The reaction was conducted under the same condition as that of Table I except the concentration of 2,6-DMP was 20%. The maximum PPO molecular weight (I.V. = 0.63 dL/g) was obtained at 35°C, and the further increase of the reaction temperature to 45°C caused a rapid decrease of PPO I.V. to 0.46 dL/g. The decrease of PPO I.V. at higher reaction temperature may be due to the loss of volatile amine.

The Role of DMBA in the Copper-Based Polymerization Catalyst

Cu/Br/DBEDA, Cu/Br/DMBA, and Cu/Br/DBEDA/DMBA complexes were used for 2,6-DMP polymerization to study the role of DMBA in the copper-based polymerization catalyst. No polymer was obtained when either Cu/Br/DBEDA or Cu/Br/DMBA was used, which means that neither DBEDA nor DMBA can act alone in promoting the copper-ion catalytic activity for 2,6-DMP polymerization. But Cu/Br/DBEDA/DMBA was a very ef-

**Figure 1** Effect of DMBA/Cu molar ratio on PPO I.V.**Figure 2** Effect of temperature on PPO I.V.

fective catalyst for 2,6-DMP polymerization, which produced PPO with 0.63 dL/g intrinsic viscosity and 99% yield. The results suggest that both amines are required for the copper-based polymerization catalyst.

Figure 3 compares the infrared spectral patterns for DBEDA (spectrum A), Cu/Br/DBEDA complex (spectrum B), and Cu/Br/DBEDA/DMBA complex (spectrum C), respectively. In spectrum A, the band at 3227.32 cm^{-1} is due to the N—H stretching vibration in the DBEDA molecules. The N—H stretching band shifted to 3395.15 cm^{-1} when the DBEDA molecules were coordinated with the copper ion, as shown in pattern B. The large shift in the N—H stretching band suggests that there is

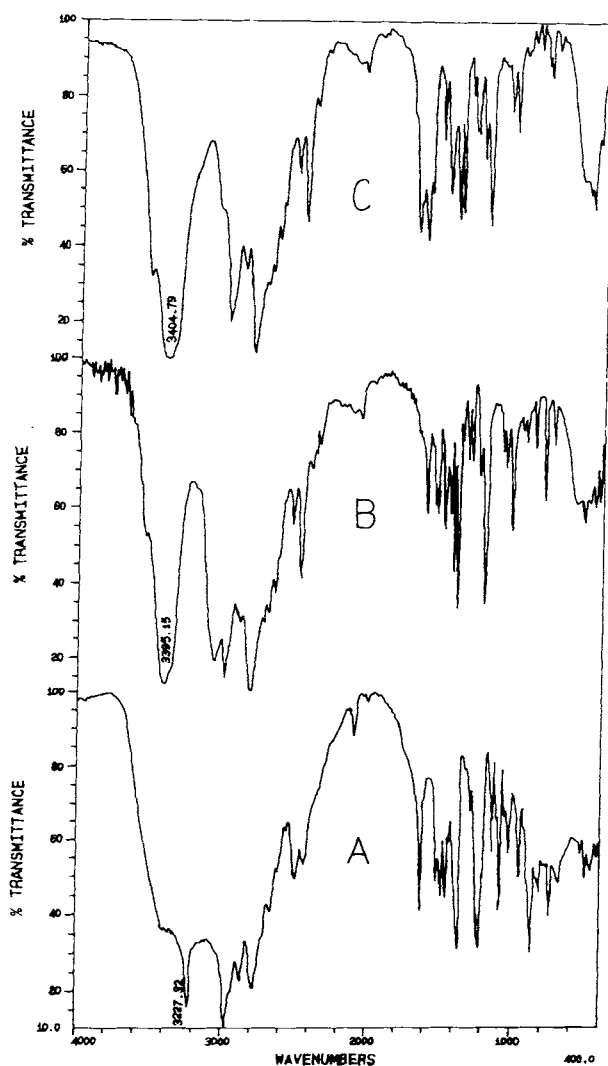


Figure 3 Comparisons of infrared spectral patterns [spectrum A, *N,N'*-di-*tert*-butylethylene diamine (DBEDA), spectrum B, Cu/Br/DBEDA complex, spectrum C, Cu/Br/DBEDA/DMBA complex].

a strong interaction between the copper ions and the N atoms in the DBEDA molecules and it is evidence of the occurrence of the ligand-copper coordination in the Cu/Br/DBEDA complex. The infrared spectral pattern in spectrum C is almost identical to that in spectrum B with only a slight shift in the band positions. Compared to spectrum B, no additional new peaks appear in spectrum C, which suggests that little DMBA existed in the dried Cu/Br/DBEDA/DMBA sample. That is, the DMBA molecule was not chemically bound to the Cu/Br/DBEDA complex (or the bonding was very weak) and, therefore, most of the DMBA molecules were removed during vacuum drying of the sample at room temperature. The reason for the no coordination between copper ions and DMBA molecules might be because the DBEDA molecules have much higher affinity for the copper ions than DMBA molecules, therefore, the metal-ligand bond existed between Cu-DBEDA only but not between Cu-DMBA. In other words, DMBA acted as the external base only for the Cu/Br/DBEDA complex; it neutralized the excess hydrobromic acid in the $\text{Cu}_2\text{O}/\text{HBr}$ solution (HBr/Cu molar ratio was five for the preparation of the polymerization catalyst). In addition, DMBA is a tertiary amine and, therefore, a quaternary ammonium compound was formed due to the reaction of DMBA with HBr. It is well known that most of the quaternary ammonium compounds are good phase transfer catalysts for reactions between organic phase and aqueous phase, therefore, the quaternary ammonium compound formed by DMBA and HBr might act as a phase transfer catalyst, which dramatically increased the 2,6-dimethylphenol polymerization rate (because the organic phase and aqueous phase coexist in the polymerization reactor).

CONCLUSIONS

Condea γ -alumina was used to catalyze the methylation of *n*-butylamine to produce a product solution which was used directly for the preparation of a 2,6-dimethylphenol polymerization catalyst. The performance of the unpurified methylation product solution from Condea γ -alumina was comparable to that of the reagent-grade *N,N*-dimethyl-*n*-butylamine, and was superior to those from other methylation catalysts. At a DMBA/Cu molar ratio of eight, the polymerization catalyst prepared with the unpurified methylation product solution still produced PPO with a molecular weight high enough for commercial use. Based on the results of infrared

measurements, the function of DMBA in the polymerization catalyst was to act as the external base which neutralized the excess hydrobromic acid in the copper-based catalyst and formed a quaternary ammonium compound to increase the polymerization rate of 2,6-dimethylphenol.

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