Polymer Bulletin 34, 419–424 (1995)

Polymer Bulletin

Oxidative polymerization of 2,6-dimethylphenol catalyzed by copper-mixed amine system

Kuo-Tseng Li

Department of Chemical Engineering, Tunghai University, Taichung, Taiwan, Republic of China

Received: 14 November 1994/Revised version: 20 December 1994/Accepted: 30 December 1994

Summary

Copper - mixed n-butylamine /dibutylamine complex was used as the catalyst for 2,6-dimethylphenol polymerization. The effects of several variables such as copper salts, additives , reaction temperature and pressure, and amine/copper ratio on the catalyst performance were studied. The catalyst activity was found to be highly dependent on the specific combination of copper salts and amines, and copper iodide - amine complex showed an unusual long induction period. Polymer molecular weight was sensitive to the addition of methanol and surfactant, reaction temperature and amine/copper ratio but insensitive to the pressure. Initial polymerization rate was strongly affected by reaction pressure.

Introduction

Polyphenylene oxide (PPO) is an important engineering polymer. The blends of PPO/polystyrene, PPO/polyamide and PPO/PBT have found a variety of commercial applications, including automotive, business machines and computer, house appliances, housings for hair drier and pump, and impellers (1).

PPO is synthesized by the copper-catalyzed oxidative coupling polymerization of 2,6-dimethylphenol (2). Various amines have been used to promote the catalytic activities of the copper based (usually copper chloride and copper bromide) polymerization catalysts, including pyridine, aliphatic diamine and dibutylamine (1).

In a previous paper (3) we used a mixture of n-butylamine and dibutylamine as the ligand for a cuprous salt-based polymerization catalyst, and observed a synergistic phenomenon for the polymerization of 2,6-dimethylphenol to PPO. That is, under identical reaction conditions, the polymer produced with the copper - mixed amine complex had much higher molecular weight than those produced with the copper - single amine complexes. This finding promoted an investigation of the variables which might affect the catalytic activity of the copper-mixed amine complex. The results of this investigation are reported in this paper.

Experimental

2,6- Dimethylphenol (2,6-DMP) was made from the methylation of phenol over a manganese catalyst (4), and had a purity of 99.94 % w/w as measured by gas chromatography. Cuprous oxide, cupric oxide (both from Showa Chemicals, Tokyo), cuprous iodide (Ferak, Berlin), hydrobromide acid (49 wt%), butylamine and dibutylamine (all from Janssen Chimica, Beligum) were used for the preparation of polymerization catalyst.

Oxidative polymerization was carried out in a 600mL PARR reactor which was immersed in a water bath. The reactor temperature and the water bath temperature were measured by J-type thermocouples. Determined amounts of catalyst solution were added to the reactor containing 15 g of 2,6-DMP and 100 g of toluene . For copper -mixed amine complex, the molar ratio of butylamine to dibutylamine was 1. Polymerization was initiated by bubbling pure oxygen through the reaction solution, the oxygen flow rate was maintained at 200 ml/min. The reaction temperature and pressure was kept at 30 °C and 1 kg/cm^2 unless stated otherwise.

After two hours of reaction, the PPO produced was precipitated with methanol, filtered, washed with methanol, and dried. Intrinsic viscosities (I.V.) of the dried PPO samples were determined from chloroform solution at 30 °C using a Ubbelode glass capillary viscometer.

Results and Discussion

(a) Effect of copper salts

Table 1 compares the PPO intrinsic viscosities obtained by using five different copper salts, including cuprous oxide/HBr ,cupric oxide/HBr (both have Br/Cu molar ratio of 5), cupric bromide, cuprous chloride, and cuprous iodide. The reaction conditions were DMP/Cu molar ratio = 236 (the molar ratio = 100 for CuI) and amine /copper molar ratio =50. For cuprous oxide / HBr and cupric oxide/HBr, the performances of copper-mixed amine complex are superior to those of copper-single amine complexes, which show the synergistic phenomena. However, there are no such synergistic phenomena observed for the cupric bromide, cuprous chloride and cuprous iodide. The comparisons between the results obtained for cupric oxide/HBr/mixed-amine complex and for cupric bromide/mixed-amine complex suggest that the presence of water in HBr solution (51 wt % of the HBr soution are water) or the pH change due to the presence of excess HBr improves the catalytic activity of copper-mixed amine complex (PPO I.V. increases from 0.51 to 0.71 dl/g) , but dramatically decreases the catalytic activity of copper-dibutylamine complex (PPO I.V. decreases from 0.7 to 0.12 dl/g). Besides, the performances of copper oxide/HBr/n-butylamine complexes are better than that of cupric bromide/ n-butylamine complex (PPO I.V. is 0.55 dl/g for the former and 0.39

Table 1 . Effect of Copper Salts on PPO I.V.

Copper Salts	n-Butylamine	Mixed Amine	Dibutylamine
Cu_2O/HBr	0.55	0.82	0.64
CuO /HBr	0.55	0.71	O.12
$CuBr_2$	0.39	0.51	0.70
CuCl	0.11	0.13	0.28
*CuI	0.62	0.11	0.11

dl/g for the latter), which suggest that the promotion effectiveness of the butylamine ligand for the 2,6-DMP polymerization catalyst can be significantly improved by the pressence of HBr solution.

Table 1 also shows that for cuprous iodide, the performance of copper - butylamine complex is much better than that of copper -dibutylamine complex (PPO I.V. =0.62 dl/g for the former compares to 0.11 dl/g for the latter). The difference may be due to the steric hindrance effect. Iodide ion is larger than bromide ion, therefore, dibutylamine is more difficult to coordinate to the copper ion in copper iodide than n-butylamine does. The results in Table 1 suggest that the affinity of copper ion for amine ligand strongly depend on the anion surrounding the copper ion , and the affinity strongly influence the stability and hence the catalytic activity of the copper-amine complexes.

An interesting finding during the study of copper salt effect is that the cupric iodide-based complexes has much longer induction period than all other catalysts studied. This phenomenon can be clearly seen from the temperature rise profiles of the reaction medium, as shown in Figure 1. Temperature rise is a good indicator of the polymerization rate because 2,6-DMP polymerization is strongly exothermic. In Figure 1, the maxium temperature rise (i.e, maximum polymerization rate) occurs at 48 minutes after the reaction started for cuprous iodide-butylamine catalyst system, but the maximum temperature rise occur at less than 5 minutes for cupric bromide -butylamine system. This unexpected behavior of the copper iodide - based catalyst system will be studied later.

Since the Cu_2O/HBr -mixed amine complex has the best performance among the catalysts listed in Table 1, the following results were obtained by using cuprous oxide/HBr as the copper salt and mixed butylamine / dibutylamine (molar ratio = 1:1) as the ligand .

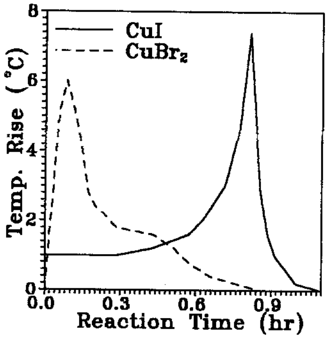

Figure 1 Reaction temperature rise vs. reaction time for CuI-butylamine and $CuBr_2$ - butylamine complexes

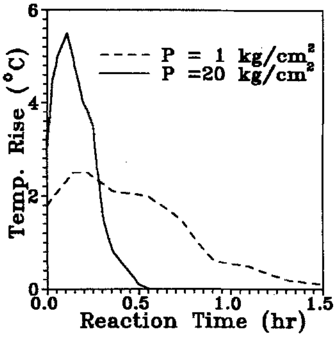

Figure 2 Reaction temperature rise vs. reaction time for P= 1 kg/cm^2 and 20 kg/cm^2

(b) Effect of reaction pressure and temperature

The effect of reaction pressure on PPO I.V. is not significant. As the reaction pressure increased from 1 Kg/cm^2 to 20 kg/cm^2, the PPO I.V. values increased only 0.05 dl/g. However, the initial polymerization rate is very sensitive to the change of reaction pressure, as shown in Figure 2. Figure 2 shows the reaction temperature rise profiles for reaction pressure at 20 kg/cm^2 and 1 kg/cm^2. It is noted that the maximum temperature rise (related to the maximum reaction rate) is 5.5 °C for 20 kg/cm^2, which is much higher than that for 1 Kg/cm ^{2} (maximum temperature rise is 2.5 °C). The results suggest that the initial stage of polymerization is strongly influenced by the mass transfer of oxygen into the reaction medium because higher oxygen pressure will increase the mass transfer rate of oxygen into the liquid phase. Under separate experiments, we have found that the initial polymerization rate can be expressed as rate $=$ a $\times$ (agitation power)^b $\times$ (superficial velocity)^c $\times$ (pressure), which clearly demonstrate that the initial rate of polymerization is controlled by the mass transfer rate of oxygen into the reaction medium.

The effect of reaction temperature on PPO I.V. was studied in the temperature range between 0 and 50 °C. The DMP/Cu molar ratio was kept at 472 and amine/copper ratio was 50. As shown in Figure 3, PPO I.V. is very sensitive to the variation of reaction temperaure, and the maximum PPO I.V. occurs at temperature around 30 °C. The decrease of PPO I.V. at higher reaction temperature is probably due to the loss of volatile free amine (5).

(c) Effect of Additives

Table 2 and 3 show the effects of additives (methanol and surfactant) on the performance of copper-mixed amine complex and copper-single amine complexes, respectively. The reaction conditions were DMP/Cu molar ratio = 472, reaction temperature = 30 °C and pressure = 1 kg/cm^2. Table 2 shows that both methanol and surfactant (methyl-tri-n-octylammonium chloride) can significantly improve the performance of copper-mixed amine complex (PPO I.V. increases from 0.42 dl/g to 0.63 dl/g for amine/copper molar ratio = 50). However, the performances of the copper-single amine complexes were almost unaffected by the addition of methanol and surfactant, as shown in Table 3. Table 2 also shows that small amount of surfactant (or phase transfer catalyst) is adequate to improve the copper - mixed amine performance (PPO I.V. increases from 0.34 to 0.41 dl/g due to the addition of surfactant/Cu molar ratio of 0.224), further increase the surfactant amount from surfactant/copper molar ratio = 0.224 to 1.0 does not have any additional advantage.

(d) Effect of amine/copper ratio

Figure 4 shows the influence of amine/copper ratio on the PPO I.V. obtained. The molar ratio of DMP/Cu was kept at 472 for the runs. As amine/copper ratio of the copper-mixed amine complex increases from 6.3 to 50, the PPO I.V. increases from 0.015 to 0.42 dl/g, which means that the performance of copper-mixed amine catalyst is strongly influenced by its amine/copper ratio. Since butylamine in the mixed amine solution is highly volatile, it is important to prevent the escape of n-butylamine from the reaction mixture during polymerization.

Table 2. Effect of Additives on Complex - Mixed Amine Complex

Amine/Copper	Methanol/Copper	Surfactant/Cu	PPO I.V. (dl/g)
30	0	0	0.29
30	60	0	0.34
30	60	0.224	0.41
30	60	1.0	0.40
50	0	0	0.42
50	120	0	0.53
50	120	0.476	0.63

Table 3. Effect of Additives on Copper - Single Amine Complexes

Amine/Copper	Methanol/Copper	Surfactant/Cu	PPO I.V. (dl/g)
(A) butylamine			
25	0	0	0.17
25	60	0.52	0.16
50	0	0	0.24
50	120	0	0.25
(B) Dibutylamine			
50	0	0	0.18
50	120	0	0.19

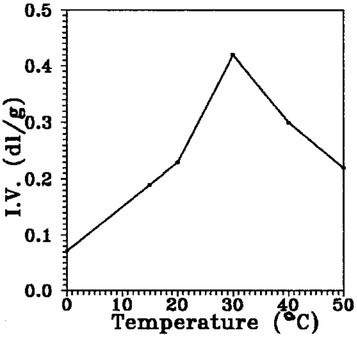

Figure 3 PPO I.V. as a function of Reaction Temperature

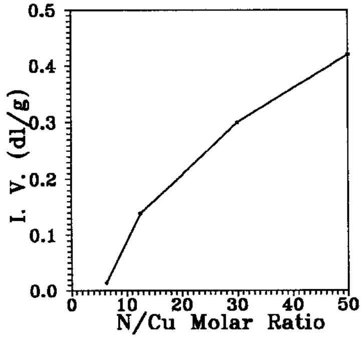

Figure 4 PPO I.V. as a function of amine/copper ratio

Conclusions

The catalytic activity of copper-mixed n-butylamine/dibutylamine complex for the oxidative polymerization of 2,6-dimethylphenol was examined. The influences of copper salts, additives, amine/copper ratio, reaction temperature and pressure on the 2,6-DMP polymerization feature and PPO properties were reported. These parameters studied showed strong effects on the performances of the copper-mixed amine catalyst.

Acknowledgment

The author thanks China Technical Consultants, Inc. for financal support.

References

1. Aycock D, Abolins V, and White DM (1988) Poly(phenylene ether). In : Mark HF, Bikales VN, Overberger CG, Menges G (eds) Encyl Poly Eng Sci, John Wiley & Sons, New York, (vol 13, pp 1-30)
2. Hay AS (1969) Macromolecules 2:107
3. Li KT , Shieh DC (1994) Ind Eng Chem Res 33: 1107
4. Li KT, Wang I, Chang KR (1993) Ind Eng Chem Res 32: 1007
5. Li KT (1994) J Appl Polym Sci 54:1339