Synthesis of Poly(2,6-Dimethyl-1,4-Phenylene Ether) Catalyzed by Copper–Diamine System

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SYNOPSIS

Oxidative polymerization of 2,6-dimethylphenol to poly(2,6-dimethyl-1,4-phenylene ether) (PPE) was studied in a high-pressure batch reactor using a copper–diamine catalyst. In the presence of air, the effect of monomer sources, catalyst formulation (copper salts, ligands, surfactant), and reaction conditions (air flow rate and pressure, temperature, agitation, monomer and catalyst concentrations) on the catalyst performance was investigated. The sensitivity of PPE molecular weight and the sensitivity of polymerization rates to these factors were found to be quite different, indicating that little correlation existed between the PPE molecular weight and the 2,6-DMP polymerization rates. Mechanical test showed that the PPE produced with the copper–diamine catalyst had modulus significantly higher than that produced with the copper–dibutylamine catalyst system. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) is one of the leading engineering resins. Its alloys are widely used in appliances, business machines, industrial equipment, automotive components, and telecommunications equipment. The polymer is prepared industrially by the oxidative polymerization of 2,6-dimethylphenol (2,6-DMP) using a copper–diamine complex as the polymerization catalyst.[1,2] The catalyst system contains copper ion, bromide ion, N,N'-di-tert-butylethylene diamine (DBEDA), N,N-dimethyl-n-butylamine (DMBA), di-n-butylamine (DBA) and a surfactant,[3] and is highly active for the production of PPE from 2,6-DMP.

Although the copper–diamine catalyst is used industrially for the manufacture of PPE, it is surprising that there is little information about the behavior of this catalyst system, with respect to the role of ligands and reaction conditions in polymerization activity and product properties. Mobley[4] studied the kinetics of 2,6-DMP polymerization with pure oxygen at a fixed copper–diamine catalyst formulation

(molar ratio of Cu : Br : DBEDA : DMBA : DBA : surfactant = 1 : 5.357 : 2.026 : 40.5 : 8.6 : 0.24). But 2,6-DMP polymerization is a step polymerization,[5] and high molecular weight PPE [the intrinsic viscosity (int. vis.) values of most commercial-grade PPE are greater than 0.4 dL/g] can be obtained only at very high conversion (at 96% 2,6-DMP conversion, PPE intrinsic viscosity is only 0.11 dL/g, as shown in Fig. 1). Therefore, there should be no direct relation between the kinetics of 2,6-DMP polymerization and the final molecular weight of PPE.

Since molecular weight is of vital importance to the polymer's physical and mechanical properties, it is the purpose of this article to study the effect of copper–diamine catalyst formulation and reaction conditions on PPE molecular weight. The aim is to provide information which helps to find the optimum operating parameters for the preparation of this polymer.

EXPERIMENTAL

The oxidative polymerization experiments were carried out in a 600-mL stirred autoclave reactor made of titanium (supplied by Parr Instruments Co.). The reactor was immersed into a constant-temperature water bath for temperature control.
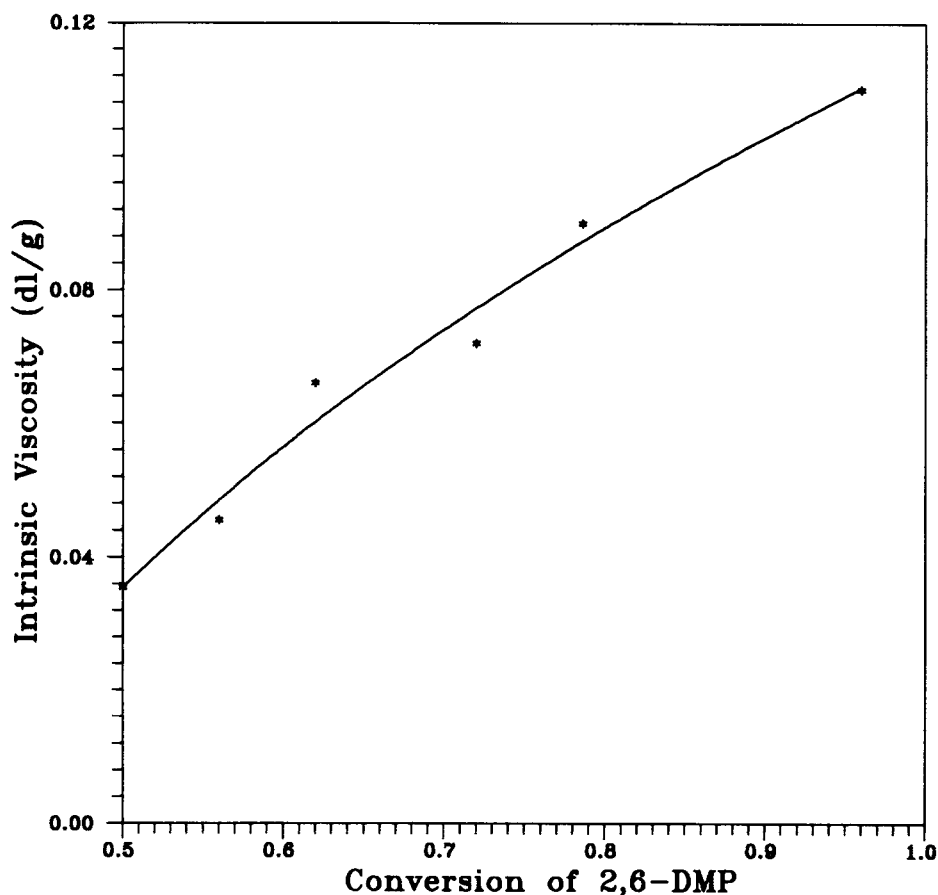
Figure 1   PPE intrinsic viscosity as a function of 2,6-DMP conversion.

In a typical experiment, a specific amount of 2,6-DMP, catalyst solution, and toluene were mixed together and charged to the reactor. After reaching the desired temperature, air was introduced through a sparger into the reactor at a desired pressure and flow rate. The composition of the exit air was analyzed periodically by a gas chromatograph (GC) equipped with a 2-m long, 80–100 mesh MS-5A column and a thermal conductivity detector. The measured exit air composition was used for the determination of polymerization rate (i.e., oxygen consumption rate) according to the following equation: Oxygen consumption rate (mL/min) = air flow rate × (inlet oxygen concentration − exit oxygen concentration).

The reaction was continued for a period of 1 or 2 h. At the end of the reaction, the reactor content was diluted with toluene and 10 mL of 2% EDTA solution was added to remove copper ions. Then the PPE produced during the reaction was precipitated with methanol. The precipitated PPE was washed with methanol and dried in a 100°C oven for 4 h.

The intrinsic viscosity (int. vis.) of the dried PPE was measured with a Schott AVS 300 system at 30°C with chloroform as the solvent.

Catalyst solution was prepared from copper salts, amines, methanol and surfactant (methyl-tri-octyl-ammonium chloride). Cuprous oxide, N,N-dimethyl-n-butylamine, and surfactant were obtained from Tokyo Kasei Kagyo Co. Ltd., Japan. N,N'-di-tert-butylethylene diamine was prepared according to the method suggested by Hay.[2] Hydrobromide acid and dibutylamine were obtained from Janssen Chimica, Belgium.

RESULTS AND DISCUSSION

Effect of Monomer Sources

Two monomer sources were used for the synthesis of PPE. One (source 1) was a purified pilot plant product, made from the methylation of phenol over a manganese catalyst.[6] The monomer had a purity

of 99.94% w/w, which was confirmed by gas chromatography. Another monomer source (source 2) was obtained from Synthetic Chemicals, U. K., with a purity of 99.85% w/w. Under identical reaction conditions, the intrinsic viscosity (int. vis.) of PPE obtained using source 1 was consistently higher than that obtained using source 2, as shown in Table I. By using Cu_2O/HBr as the copper salt, the PPE int. vis. is 0.68 dL/g for source 1 and 0.61 dL/g for source 2. By using $CuBr_2$ as the copper salt, the PPE int. vis. is 0.57 dL/g for source 1 and 0.5 dL/g for source 2. The results suggest that a small difference in monomer purity can have significant effect on the PPE int. vis. Because of its higher purity and higher PPE int. vis. obtained, the pilot plant 2,6-DMP was used for the following studies.

Effect of Catalyst Formulation

The catalyst formulation (copper salts, amine/copper ratios, surfactant) was studied using a reaction condition of 25°C, 10 kg/cm^2 pressure, 0.5 L/min air flow rate, 750 rpm agitation speed, 20% w/w monomer concentration, and 2 h reaction time. The molar ratio of 2,6-DMP : Copper : Br : DBEDA : DMBA : DBA : surfactant : methanol = 870 : 1 : 2.5 : 2 : 20 : 8 : 0.25 : 100, unless specified otherwise.

Effect of Copper Salts

Five copper salts were used, including Cu_2O/HBr (Br/Cu molar ratio = 2.5), $CuBr_2$, $CuCl_2 \cdot 2H_2O$/NaBr (Br/Cu = 2.5), (CuCl + $CuCl_2 \cdot 2H_2O$)/NaBr (Br/Cu = 2.5), and CuI. Table II compares the PPE int. vis. obtained by using these copper salts. Among the five copper salts tested, Cu_2O/HBr is the best one, producing PPE with int. vis. significantly higher than $CuBr_2$ does. The same results were also observed in Table I. However, Figure 2 shows that the

Table I Effect of Monomer Sources on PPE Intrinsic Viscosity

	Pilot Plant 2,6-DMP	Synthetic 2,6-DMP
Cu_2O/HBr (Br/Cu = 2.5)	0.68 dL/g	0.61 dL/g
$CuBr_2$	0.57 dL/g	0.5 dL/g

The 250-g reaction solution with 20 wt % monomer concentration, air pressure = 10 kg/cm^2, air flow rate = 0.5 L/min, temperature = 25°C, agitation speed = 850 rpm, reaction time = 2 hr, molar ratio of 2,6-DMP : copper : DBEDA : DMBA : DBA : surfactant : methanol = 870 : 1 : 2 : 20 : 7.4 : 0.25 : 100.

Table II Effect of Copper Salts

Copper Salts	Intrinsic Viscosity (dL/g)
Cu_2O + HBr	0.68
$CuBr_2$	0.57
$CuCl_2 \cdot 2 H_2O$/NaBr	0.63
(CuCl + $CuCl_2 \cdot 2 H_2O$)/NaBr	0.61
CuI	0.06

X-ray diffraction (XRD) pattern of dried Cu_2O/HBr is almost identical to that of $CuBr_2$, which suggests that the mixing of Cu_2O and HBr generates $CuBr_2$ and H_2O. The reason for the better performance of Cu_2O/HBr compared to $CuBr_2$ may be due to the higher Br/Cu ratio in Cu_2O/HBr mixture than that in $CuBr_2$. But the further increase of Br/Cu ratio from 2.5 to 5.0 for Cu_2O/HBr had little effect on PPE intrinsic viscosity.

Figure 3 compares the oxygen consumption rate between Cu_2O/HBr and $CuBr_2$. There are very little differences in the polymerization rates between these two copper salts; however, the difference in PPE int. vis. is significant, as shown in Table I.

The catalytic activity of copper chloride is known to be inferior to that of copper bromide for the polymerization of 2,6-DMP. Table II shows that the addition of NaBr promotes the performance of copper chloride significantly, which produces PPE with an int. vis. value comparable to that produced with Cu_2O/HBr. Among the copper salts tested, the catalytic activity of cuprous iodide was the worst.

Ratio of Amine to Copper

There are three amines in the catalyst system: DBEDA, DMBA, and DBA. The effect of DMBA and DBA on catalyst performance was investigated because they are used in much greater quantities than DBEDA. The results are shown in Table III.

Without the presence of DMBA, little PPE was formed, and the dominant product was 3,3',5,5'-tetramethyldiphenoquinone which is the by-product of 2,6-DMP oxidative coupling (i.e., the product due to C — C coupling instead of C — O coupling). As the DMBA/copper molar ratio increased, the PPE int. vis. increased but became almost constant at DMBA/copper = 10 or 20.

For DBA, a pronounced drop of PPE int. vis. (from 0.68 to 0.21 dL/g) is observed when DBA was absent from the catalyst system. Although DBA has

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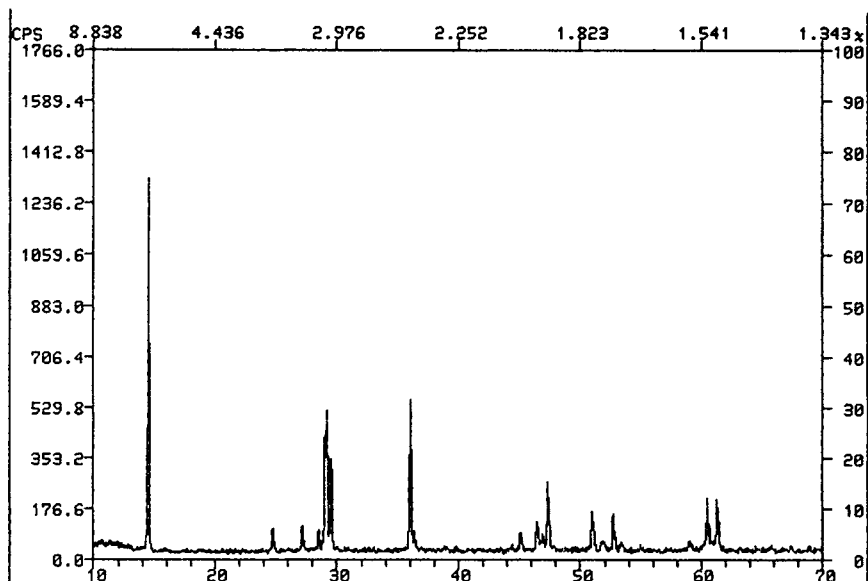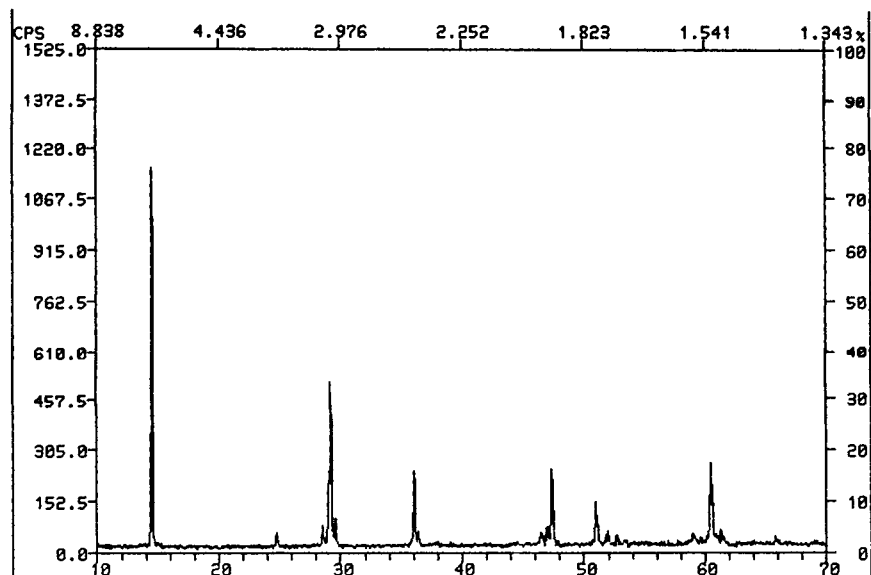
(b)

Figure 2   XRD spectra of (a) cupric bromide, and (b) dried cuprous oxide/hydrobromide acid mixture.
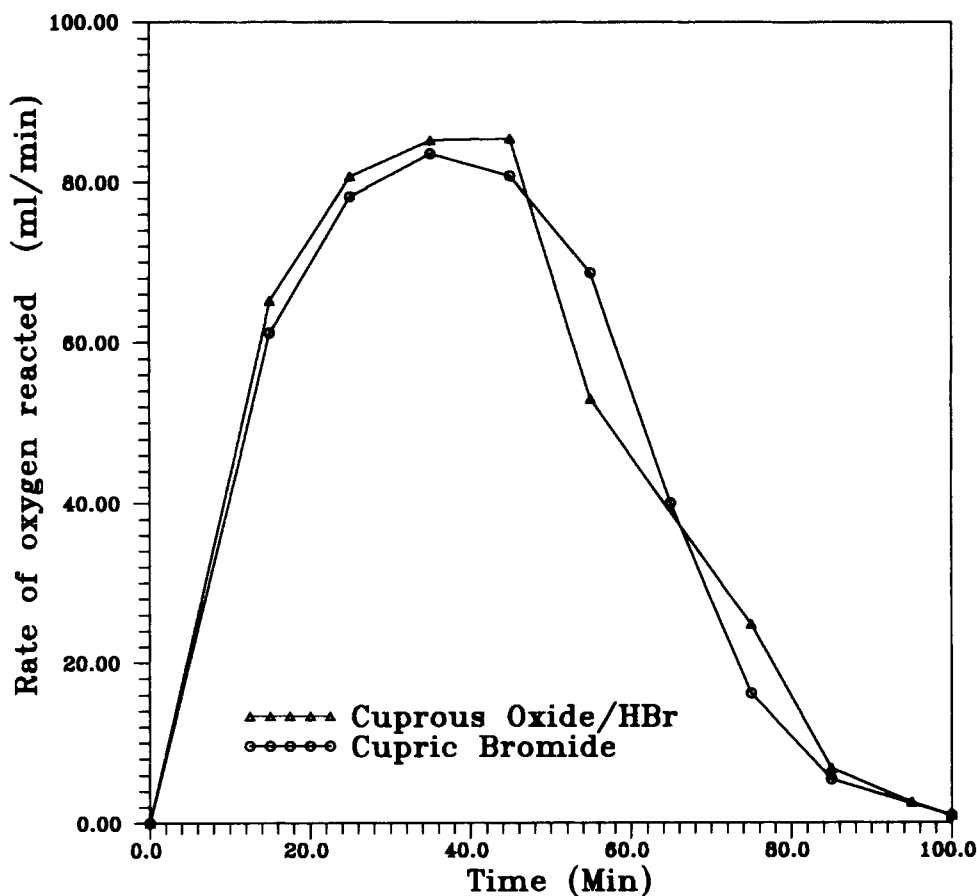
Figure 3 Effect of copper salts on polymerization rate.

great effect on PPE int. vis., it has little effect on the polymerization rate, as shown in Figure 4. Figure 4 indicates that the oxygen consumption rate changes little in the absence of DBA.

Effect of Surfactant

Figure 5 shows the effect of surfactant on the PPE int. vis. In the range of surfactant/copper molar

Table III   Effect of Amine/Copper Ratio

DMBA/Cu Molar Ratio	DBA/Cu Molar Ratio	Intrinsic Viscosity (dL/g)
0	8	0
5	8	0.53
10	8	0.65
20	8	0.68
20	0	0.21

ratio between 0 and 0.25, the increase of surfactant concentration significantly increases the PPE int. vis. However, the analysis of exit air composition found that the effect of surfactant on polymerization rate was not significant.

Effect of Reaction Conditions

A series of experiments was performed under different reaction conditions to study the effect of the following factors on PPE int. vis. and polymerization rates: air flow rate and agitation speed, air pressure, temperature, monomer/copper ratio and reaction time, monomer concentration. A catalyst formulation of molar ratio of Cu : Br : DBEDA : DMBA : DBA : surfactant : methanol = 1 : 2 : 1.8 : 10 : 7.4 : 0.24 : 90 was used. With the exception of the experiments concerning the effect of monomer/copper ratio, all experiments were performed at a 2,6-DMP/copper molar ratio of 780.

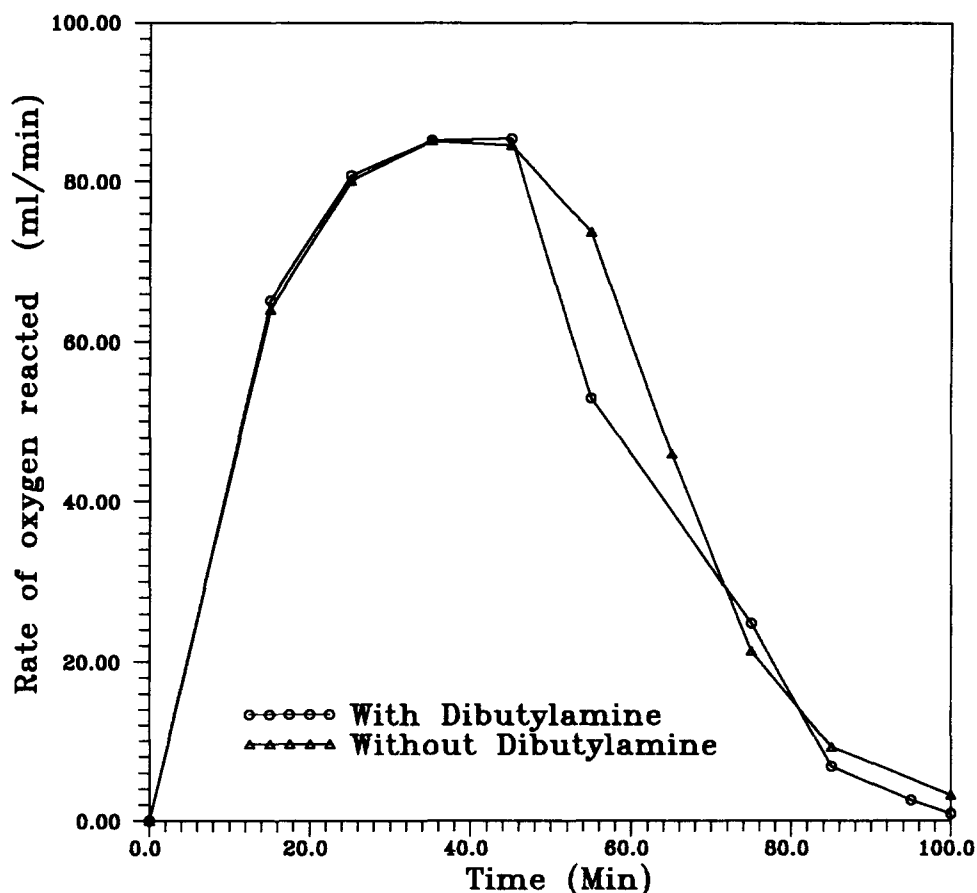**Figure 4** Effect of DBA on polymerization rate.

Air Flow Rate and Agitation Speed

The influence of air flow rate on 2,6-DMP polymerization was studied in a range of 0.2 L/min to 5 L/min. The data in Figure 6 show that the PPE int. vis. values remain essentially unchanged when the air flow rate increases 25 times. The slightly lower intrinsic viscosity at high air flow rate may be due to the fact that some amines were carried away from the reactor at high air flow rate, which decreases the amine/copper ratio.

On the other hand, varying the air flow rate shows a dramatic change in the polymerization rate, as reported in Figure 7. At the initial polymerization stage, the reaction rate of 5 L/min flow rate is much higher than that of 0.5 L/min flow rate, indicating the existence of very strong mass-transfer limitation at the low air flow rate range.

At 5 L/min air flow rate, experiments were run at four different agitation speeds. As shown in Table IV, the change of impeller agitation speed has little effect on the PPE int. vis. But the polymerization rate is strongly influenced by the agitation speed,

as shown in Figure 8. It is expected that the effect of agitation speed on polymerization rate will be more pronounced when the air flow rate decreases.

The results in Table IV and Figures 6–8 suggest that there is no definite relationship between the polymerization rate and polymer molecular weight. A large difference in polymerization rate doesn't necessarily result in a significant difference in PPE int. vis. obtained. In fact, a lower polymerization rate can sometimes even result in higher PPE int. vis., as shown in Figures 6 and 7.

Influence of Pressure

The results obtained between 1 and 20 kg/cm^2 pressure are reported in Figure 9 for 2,6-DMP polymerization (air flow rate = 0.2 L/min, 850 rpm agitation speed, 10 wt % monomer concentration, 15°C, and 2 h reaction time). At low pressure range, PPE int. vis. is highly sensitive to air pressure, which increases from 0.3 to 0.55 dL/g as pressure increases from 1 to 5 kg/cm^2. But the sensitivity decreases significantly at higher pressure range. The PPE int.
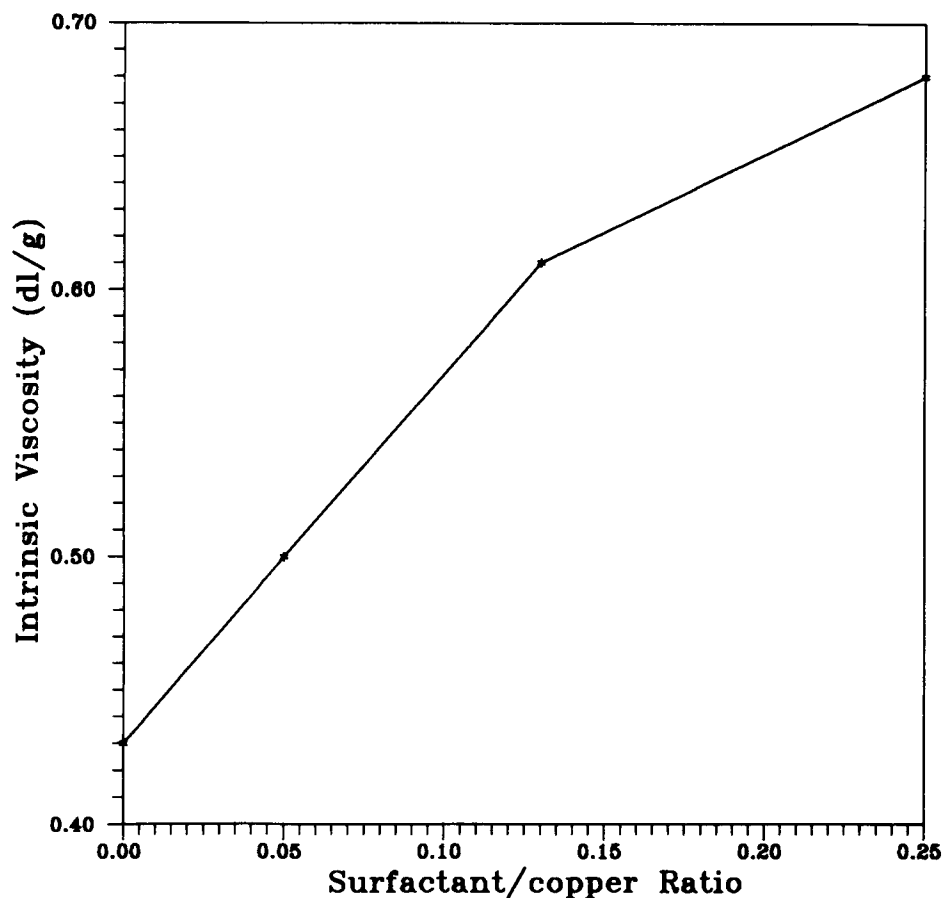
Figure 5   Effect of surfactant on PPE intrinsic viscosity.

vis. increases only 0.09 dL/g for a pressure increase from 5 to 20 kg/cm².

Temperature

Five sets of experiments were conducted to study the effect of temperature from 15 to 45°C on 2,6-DMP polymerization. Figure 10 shows the variation of PPE int. vis. as a function of temperature. Considerable differences in the PPE int. vis. are observed in the temperature range of 0–45°C. Intrinsic viscosity increases with the increase of temperature between 0 and 15°C, while int. vis. decreases rapidly as temperature increases from 15 to 45°C. The results in Figure 10 clearly demonstrate the sensitivity of PPE int. vis. to temperature, and suggests that proper temperature control is important for the synthesis of PPE.

Mobley[4] measured PPE int. vis. at two temperatures (24.5°C and 40°C), and also found that the int. vis. value at 40°C was much lower than that at 24.5°C. He suggested that the decrease of int. vis.

at higher reaction temperature may be due to the decrease of oxygen solubility in the reaction mixture. However, the effect of temperature on the oxygen consumption rate is not strong enough (as shown in Fig. 11) to cause the rapid decrease of int. vis. from 0.4 dL/g at 25°C to 0.1 dL/g at 45°C. Therefore, the decrease of int. vis. at higher reaction temperature should be largely due to the loss of volatile amine (N,N-dimethyl-n-butylamine is highly volatible) at high reaction temperature, which results in the lower amine/copper ratio and, hence, the lower PPE intrinsic viscosity.

Monomer/Copper Ratio and Reaction Time

The effect of monomer/copper ratio on the PPE int. vis. was investigated in the range from 390 to 1,170. The polymerization was carried out at 15°C, 5 kg/cm², 0.2 L/min air flow rate and 1-h polymerization time with 20% w/w 2,6-DMP concentration. The results are presented in Figure 12. As the 2,6-DMP/copper molar ratio increased from 390
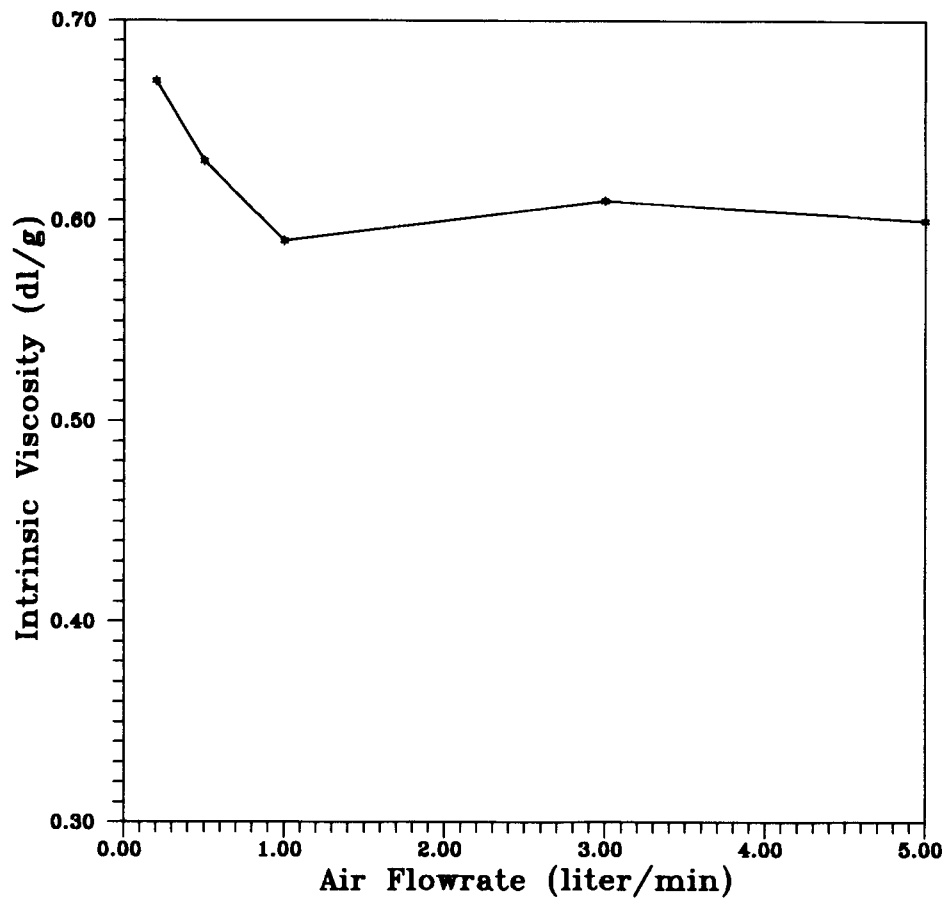
Figure 6 Effect of air flow rate on PPE intrinsic viscosity: 10% monomer concentration, 850 rpm agitation speed, 10 kg/cm² pressure, 15°C, 2-h reaction time, 100 g reaction solution.
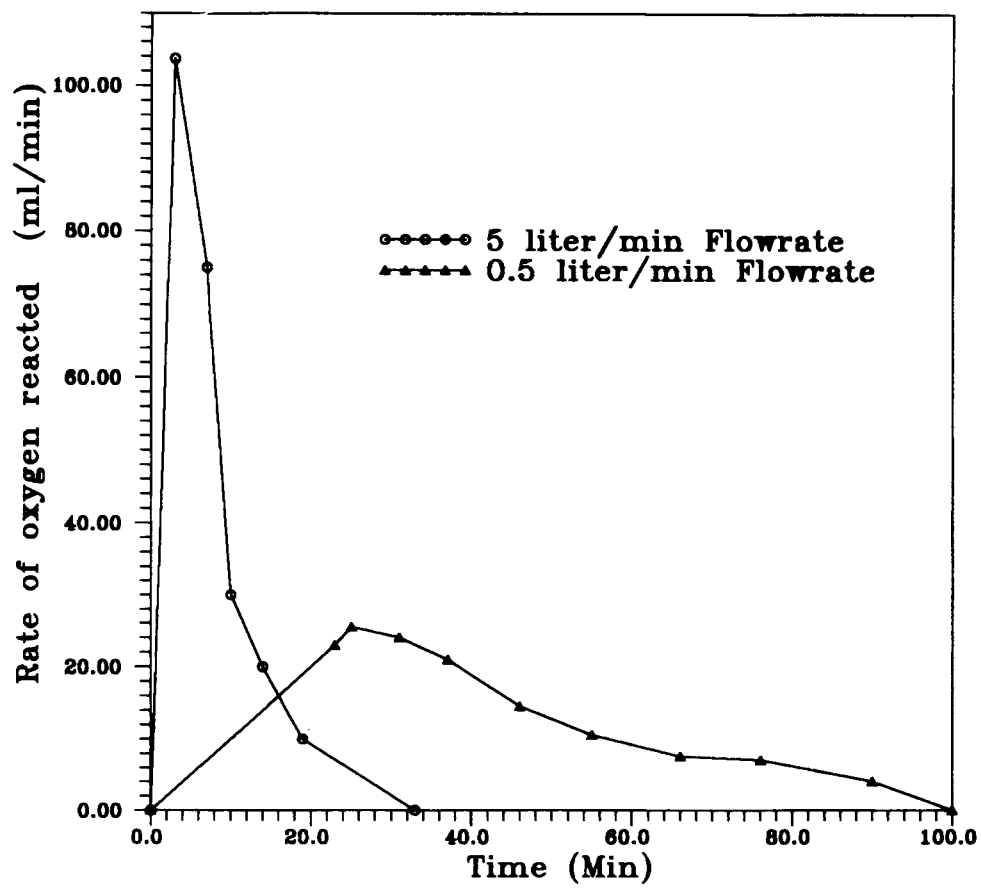
Figure 7 Effect of air flow rate on polymerization rate.

Table IV Effect of Agitation Speed on PPE Intrinsic Viscosity

Agitation Speed (rpm)	Intrinsic Viscosity (dL/g)
150	0.63
300	0.62
450	0.59
850	0.59

Air flow rate = 5 L/min, monomer concentration = 10 wt %, T = 15°C, air pressure = 20 kg/cm², reaction time = 2 h.

to 1,170, the PPE int. vis. decreased from 0.71 dL/g to 0.056 dL/g, which clearly showed the importance of the DMP/copper molar ratio in controlling the polymer molecular weight.

Figure 13 shows the change of PPE int. vis. as a function of reaction time. The intrinsic viscosity values increase steadily with an increase in reaction time. The trends of the curves in Figures 12 and 13 are opposite each other; therefore, the combination

of DMP/copper molar ratio and reaction time can be properly tuned to meet the market demand and plant capacity. For example, at the time of low market demand for PPE, the use of higher 2,6-DMP/copper ratio (i.e., lower catalyst concentration) and longer reaction time can also achieve the desired int. vis. value.

Effect of Initial Monomer Concentration

Four experiments under different initial monomer concentrations (5 wt % to 20 wt %) were conducted at 25°C, 10 kg/cm², 850 rpm, 2 L/min air flow rate, and 2-h reaction time. The results are reported in Figure 14, which shows that the higher monomer concentration results in the higher intrinsic viscosity.

Because a higher initial monomer concentration will also increase the production rate of the by-product (diphenoquinone), the optimum monomer concentration should be chosen based on the compromise between the polymerization rate (C—O coupling) and by-product formation rate (C—C coupling).
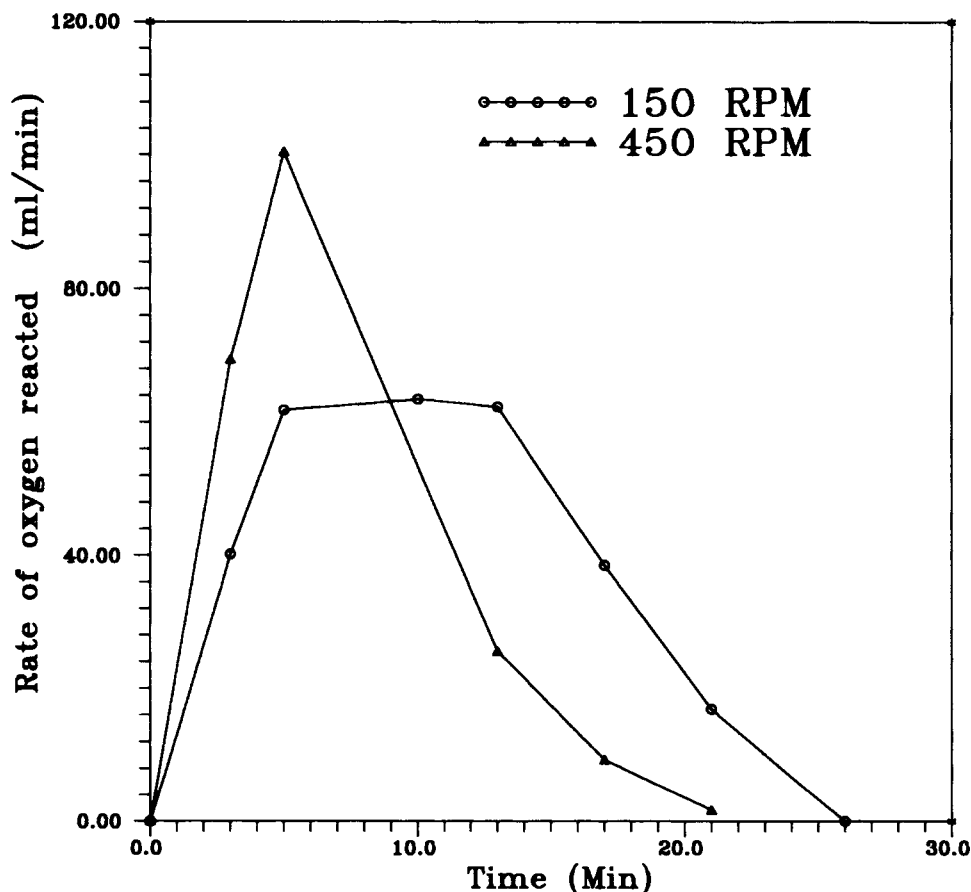
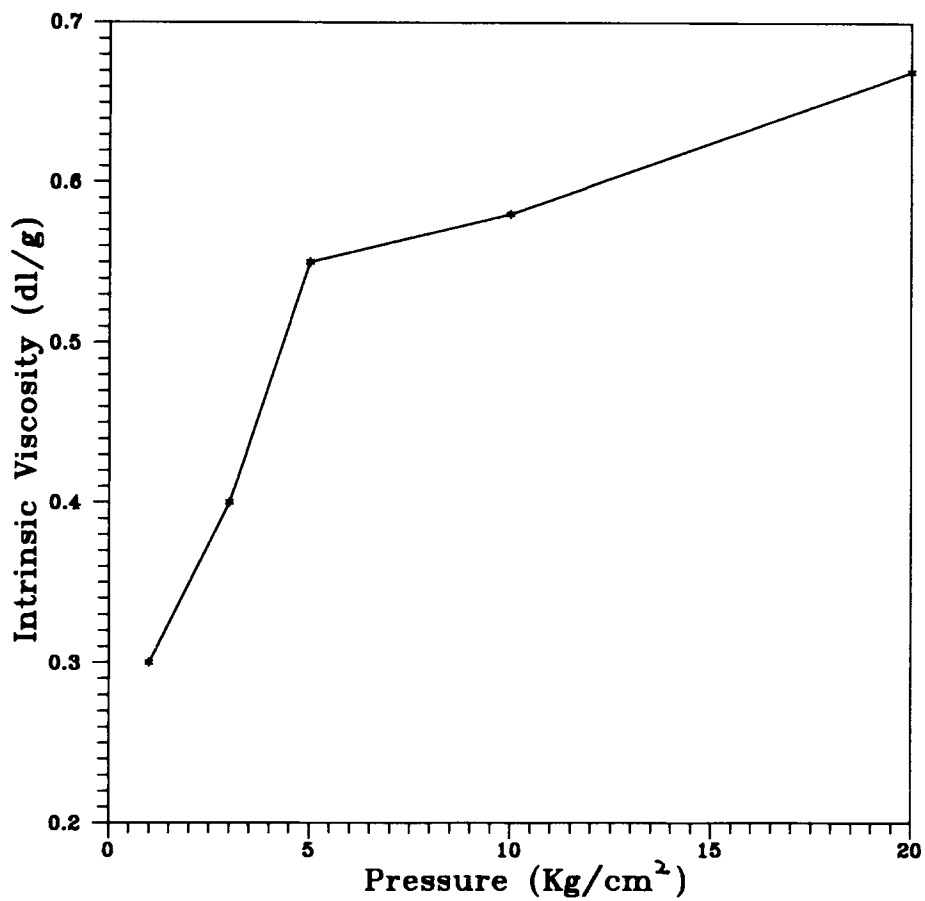**Figure 8** Influence of agitation speed on polymerization rate.

Figure 9   Influence of pressure on PPE intrinsic viscosity.
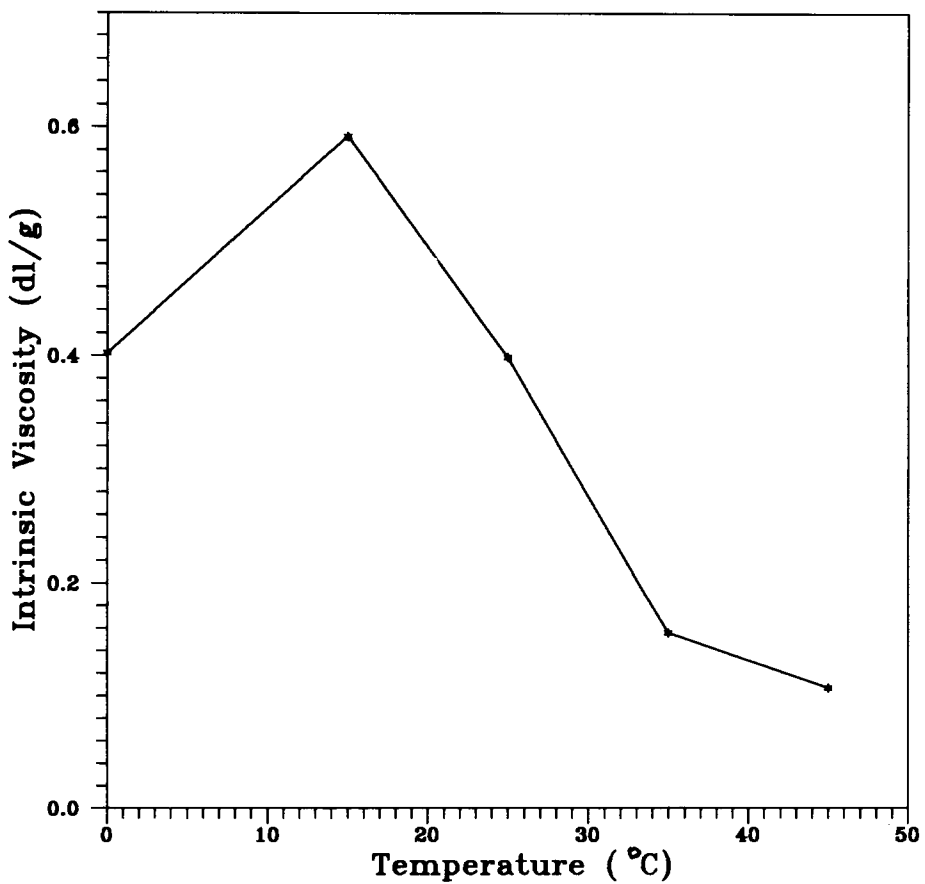

Figure 10   Effect of temperature on PPE intrinsic viscosity. (Same reaction condition as in Fig. 6 except 2 L/min flow rate and varied temperature.)
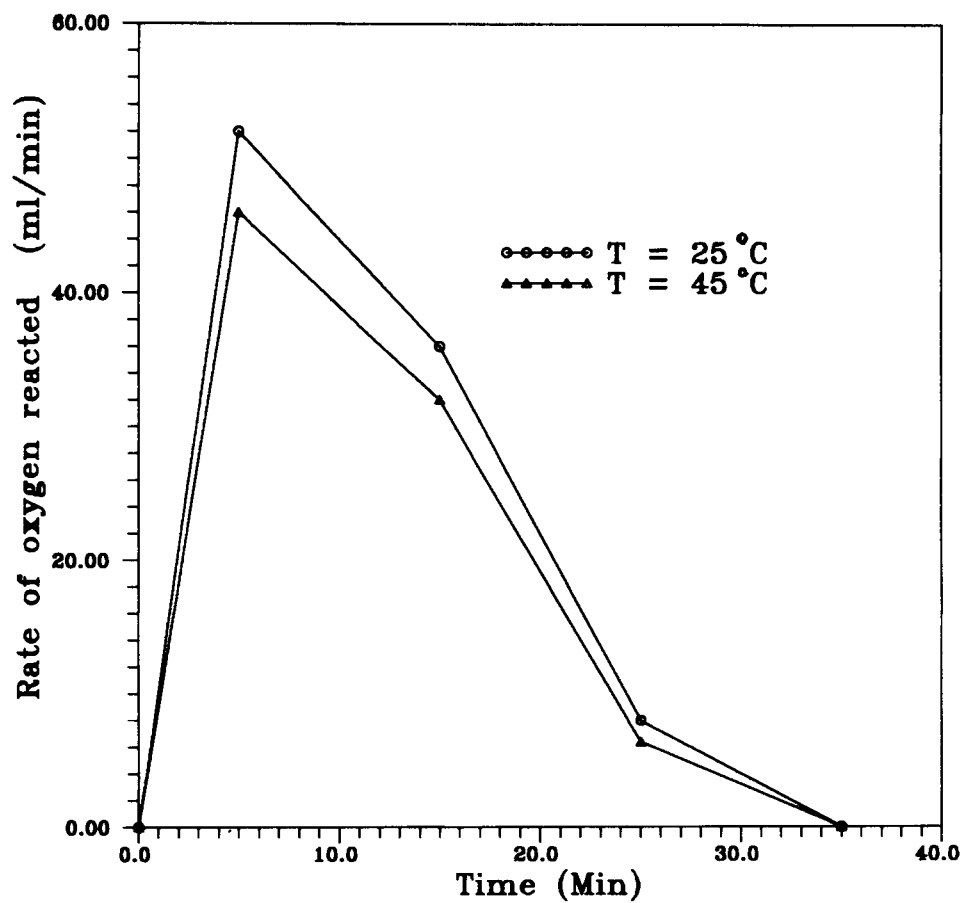
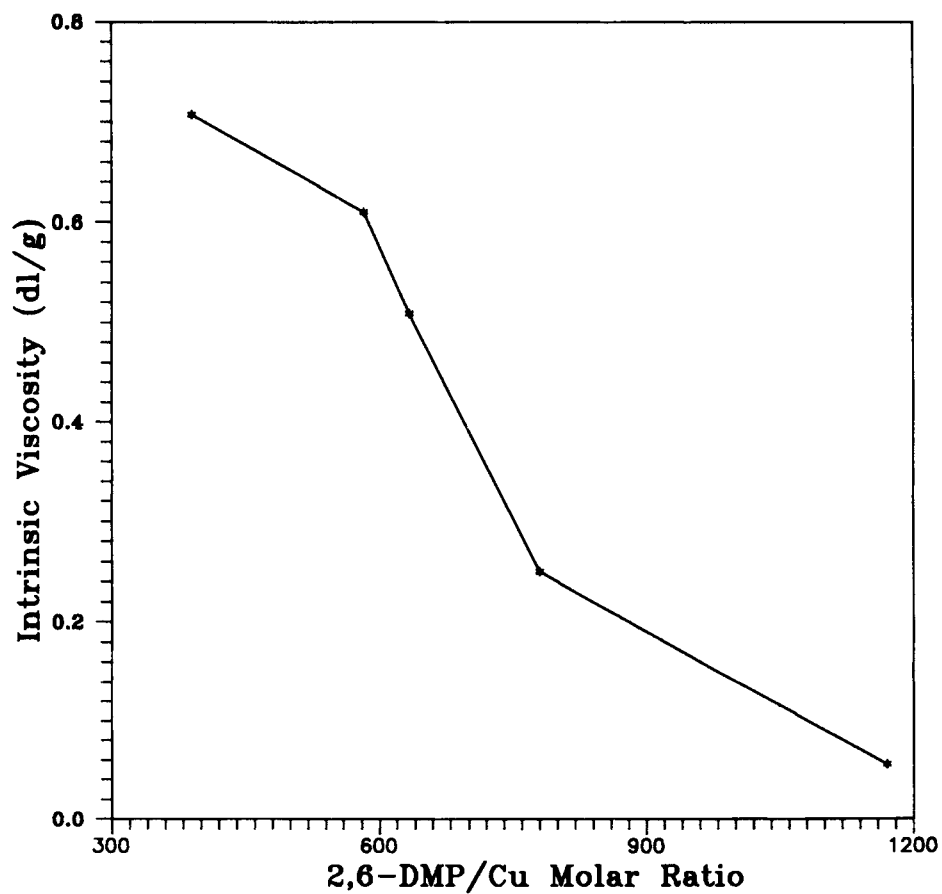**Figure 11** Effect of temperature on polymerization rate.

Figure 12 Influence of monomer/copper ratio on PPE intrinsic viscosity.
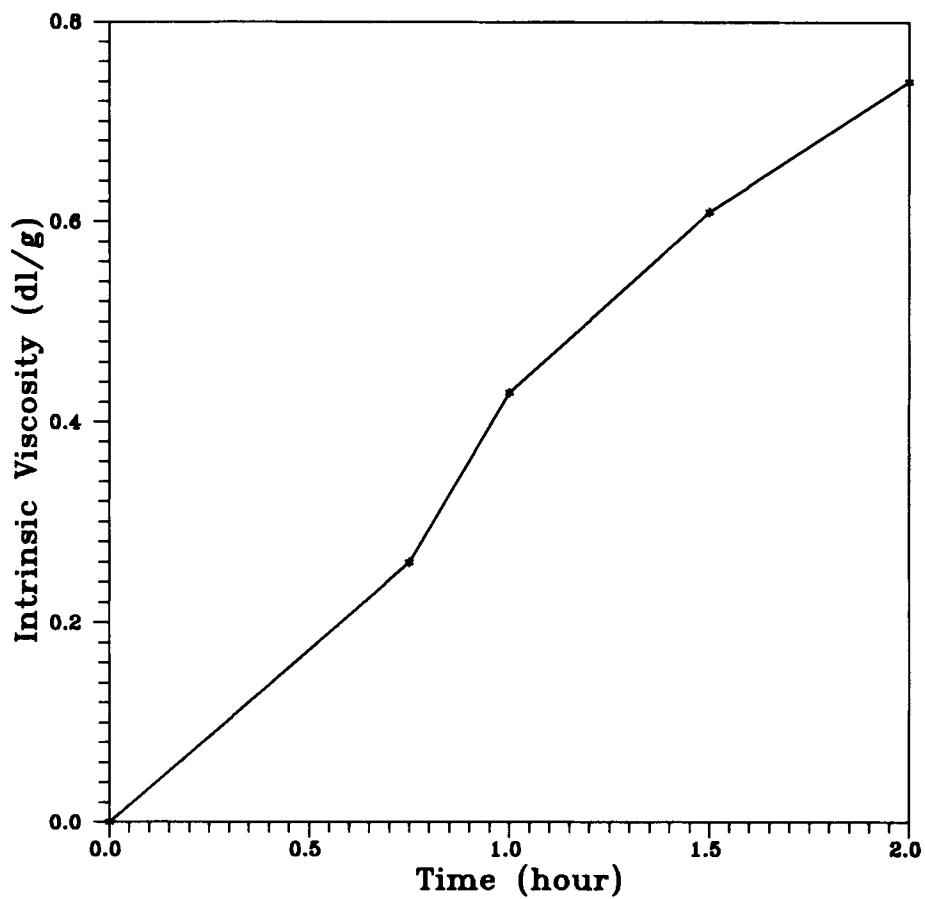
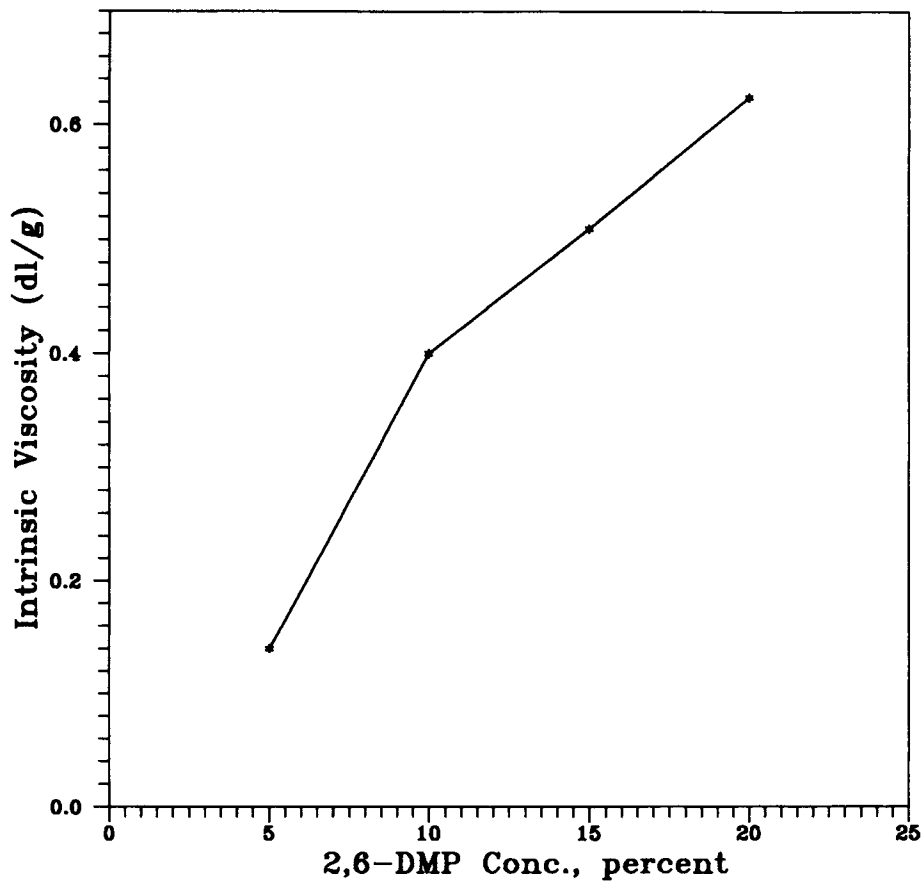**Figure 13** Variation of PPE intrinsic viscosity with reaction time.

Figure 14 PPE intrinsic viscosity vs initial monomer concentration.

Table V Effect of Catalyst System on the Mechanical Properties of Polyphenylene Ether

Catalyst	Copper–Diamine	Copper–Dibutylamine
Intrinsic viscosity (dL/g)	0.45	0.45
Tensile modulus (kg/cm²)	21,840	16,730
Tensile strength (kg/cm²)	518	490
Iod impact (ft-lb/in)	2.16	2.29
Elongation at break	21.1%	21.1%
HDT (°C)	110.7	106.7

Testing bar formulation: polyphenylene ether 50 phr, polystyrene 50 phr, TiO_2 2 phr.

Mechanical Test

To compare the mechanical properties of PPE obtained from different catalyst systems, PPE was blended with high-impact styrene and titanium oxide using a twin-screw extruder, and test bars were then prepared using an injection molding machine. Table V compares the mechanical properties between PPE obtained using two different catalyst systems (copper–diamine catalyst system and copper bromide–dibutylamine catalyst system). Among the mechanical properties tested, the most significant difference between the two samples is tensile modulus. At the same molecular weight, the PPE produced with the copper–diamine system has a tensile modulus much higher than that produced with the copper–dibutylamine system. However, other mechanical properties between the two samples are similar to each other.

CONCLUSIONS

The influence of the monomer purity, copper–diamine catalyst formulation, and reaction conditions on the synthesis of PPE from the oxidative polymerization of 2,6-DMP with air has been presented. Factors affecting the oxygen transfer rates (e.g., air flow rate and agitation) have a strong effect on the polymerization rate, but show little effect on the PPE intrinsic viscosity. However, factors affecting the liquid composition of the reaction mixture (e.g.,

monomer concentration, monomer/copper ratio, catalyst formulation, and monomer purity) have a strong effect on the PPE int. vis., but sometimes have little effect on the polymerization rates. That is, no direct relationships exist between PPE intrinsic viscosity and polymerization rates. A optimum temperature at around 15°C was found for obtaining the highest PPE int. vis. In addition, PPE produced with a copper–diamine catalyst has significantly higher modulus compared to that produced with a copper–dibutylamine catalyst.

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