

Biphasic coupling polymerization of 2,6-dimethylphenol using surface-active copper complex catalysts

Y.M. Chung^a, W.S. Ahn^{a,*}, P.K. Lim^b

^a Department of Chemical Engineering, Inha University, Incheon 402-751, South Korea

^b Department of Chemical Engineering, North Carolina State University, Raleigh, NC 27695-7905, USA

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Abstract

Coupling polymerization of 2,6-dimethylphenol to poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was carried out in an 1:1 aqueous–chloroform biphasic mixture using Cu–surface active ligand complex catalysts. Bidentate ligands were superior to monodentate ligands in promoting the oxidative coupling possibly due to their higher surface-activity and ability to form a binuclear complex with two metal ions. In particular, *N,N*-dibutylethylenediamine complex of copper gave the highest reaction rates and produced a polymer with an average molecular weight of 48,000 in a 95% yield. Spontaneous phase separation induced by the surface-active ligand made it possible to recover the catalyst complex segregated at the middle emulsion layer in a compact form. Biphasic reaction with a suitable surface-active ligand was found to be more effective than homogeneous counterpart to promote the oxidative coupling reaction and was more favorable for forming higher molecular weight polymer products. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In a conventional liquid-phase synthesis, an organic solvent typically takes on multiple functions that may include: (1) solubilizing the reactant(s), catalyst, or intermediate product(s) of the reaction, (2) serving as a catalyst ligand and promoting the desired reaction through an electronic or steric effect at the catalyst, and (3) acting as an acid or base. These functional requirements severely restrict the choice of the solvent candidates to those which are often toxic, hazardous or environmentally troublesome. In a biphasic synthesis, the functional requirements of the reaction medium are decoupled and separately assigned to aqueous and organic phases. By relieving the organic solvent of those functions that can be better handled by the aqueous phase, such as catalyst solubilization, ionization, and charge accommodation, the biphasic technique broadens the solvent choice and

* Corresponding author. Tel.: +82-32-860-7466; Fax: +82-32-872-0959; E-mail: whasahn@dragon.inha.ac.kr

improves the chances of finding a safer and more benign solvent. A surface-active ligand or complexing agent is then used to draw the catalyst to the organic–water (O–W) interface where it effects the desired reaction. Aside from an increased environmental safety, the biphasic synthesis that is based on the use of a surface-active catalyst complex can also offer other significant advantages over the homogeneous synthesis: ease of catalyst recovery and separation of product and substrate, and the attainment of high reactivity, selectivity and reproducibility under mild reaction conditions [1,2].

In this work, O–W biphasic synthesis technique has been extended to the oxidative coupling synthesis of poly(2,6-dimethyl-1,4-phenylene oxide) (hereafter PPO), a commercially important thermoplastic using 2,6-dimethylphenol as substrate. The single phase synthesis of PPO has been extensively studied [3–11], and the solvent of choice until recently has been pyridine. The solvent efficiently fulfills the following functions: (i) solubilizing the catalyst (cuprous chloride), substrate (2,6-dimethyl phenol) and intermediate products (oligomers), (ii) deprotonating the substrate to form the reactive phenoxide ion, and (iii) serving as a catalyst ligand. Unfortunately, pyridine is highly toxic, noxious, and troublesome. We have chosen chloroform as an organic liquid conveniently due to its high solubility for both the substrate and products of the synthesis reaction. It is the first time to use a dense organic liquid and a bidentate surface-active ligand in conjunction with the aqueous phase and an emulsifier to promote an interfacial synthesis reaction. We have also conducted a series of single phase synthesis experiments for comparison purposes, and demonstrated some important features of the biphasic reactions of PPO synthesis.

2. Experimental

The reaction was carried out batchwise at 1 atm in a 500 ml three-necked flask reactor using chloroform–water as the biphasic mixture, a cuprous chloride–*N,N*-dibutylethylenediamine complex as the surface-active coupling catalyst, ammonia as the base to deprotonate the substrate 2,6-dimethylphenol, sodium chloride as a solubility enhancer for cuprous chloride through chloride complexation [12], and dodecyl sulfate, sodium salt (DSS) as the emulsifier with vigorous mechanical stirring. The reactor was charged with 200 ml of a 1:1 (by volume) chloroform–aqueous solution mixture and the desired amount of the reaction ingredients, except for the catalyst. The reactor was placed in the constant-temperature water bath and purged with oxygen for about 10 min and then allowed to equilibrate to the set temperature, which was typically 25°C. The catalyst, cuprous chloride, was then added finally. After the reaction was initiated by starting the mechanical stirrer, the amount of oxygen uptake was monitored using a constant-pressure manometric unit to which the reactor is hooked up. The experimental apparatus used in this work is similar to that employed in our earlier study on the biphasic autoxidation of tetralin [2]. A similar procedure was used to carry out the homogeneous reaction, except that no emulsifier was used and the biphasic reaction medium was replaced by chloroform or pyridine.

After completion of the reaction, the reaction mixture was emptied into a separating funnel. Upon standing overnight, the organic and aqueous phase were separated out with an emulsion layer formed in between the light aqueous phase at the top and the dense organic phase at the bottom. Each of three portions was carefully separated and slowly dropped to excess volume of methanol solution containing approximately 1% hydrochloric acid with stirring. The precipitated polymer was filtered off, washed with methanol, and dried under vacuum at 65°C. After weighing the product, further

purification was performed by redissolving the solid product in chloroform and reprecipitating it in acidified methanol. The purified product was obtained after it was dried.

Identification and characterization of the purified products were conducted using FT-IR and ^1H NMR spectroscopies. The molecular weight distribution of the product was measured using GPC (gel permeation chromatography) equipped with Styragel 4T/3T GPC column and a RI (refractive index) detector at 45°C . The mobile phase was toluene maintained at a flow rate of 1.0 ml/min. The column was calibrated with polyethylene molecular weight standards.

The distribution of the copper complex in the reaction mixture was determined by analyzing the metal concentrations in the aqueous, organic, and middle emulsion layer using SHIMADZU ICPS-1000IV ICP emission spectroscopy. For the ICP analyses, it was necessary to extract the copper from the organic or emulsion samples and transfer each into an aqueous solution. After separating the polymer in advance by precipitating it in acidified methanol and filtering it, the copper containing solution was carefully evaporated to remove the solvent and the residue was digested in a concentrated nitric acid using CEM microwave sample preparation system set at 50°C and 40 psi for a duration of 10 min.

3. Results and discussion

3.1. General features of biphasic PPO synthesis

The optimum set of reaction conditions for the biphasic synthesis of PPO is summarized in Table 1. Since interfacial reactions are strongly dependent on the interfacial area, they are sensitive to parameters such as O–W volume ratio and the degree of emulsification. Because organic liquids dissolve the substrate and generally have higher solubilities for gases than water, the existence of an organic phase can significantly increase the solubility of a gaseous reactant and lead to faster reaction rate. But, increasing O–W phase ratio would decrease the concentration of monomer in the organic phase, as well as reducing the O–W interfacial area. Decreasing O–W phase ratio, while it could increase the monomer concentration in the organic phase, would also lead to decrease in the O–W interfacial area as well. In this regard, O–W phase ratio of 1:1 (or thereabout) which balances between two opposing factors was found to be the optimum. Stirring speed and emulsifier concentra-

Table 1
Optimum reaction conditions for the oxidative coupling of 2,6-dimethylphenol

Kinetic parameter	Specification
Total pressure	760 mm Hg
Reaction temperature	25°C
Stirring speed	1500 rpm
Organic phase (chloroform) volume	100 ml
Aqueous phase volume	100 ml
[CuCl]	0.025 M
[DBEDA] ^a	0.075 M
[2,6-Dimethylphenol]	0.18 M
[DSS] ^b	0.015 M
[NH ₄ OH] ^c	0.26 M

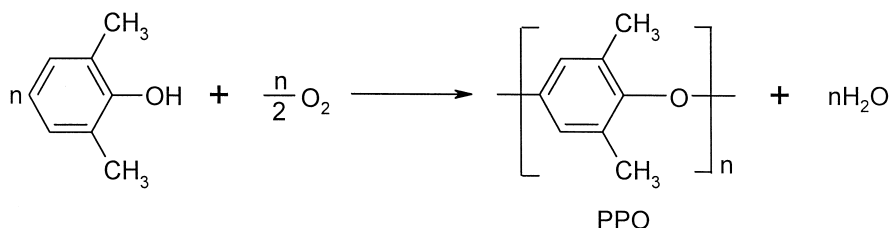
^a Dibutylethylenediamine.

^b Dodecyl sodium sulfate.

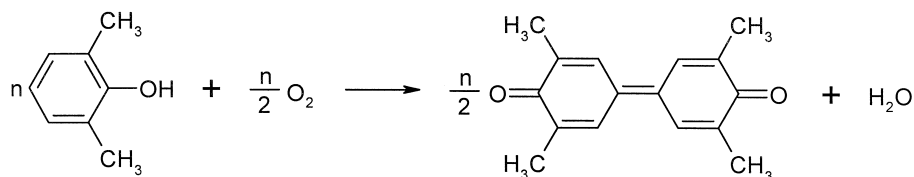
^c 28% NH₃ in water.

tion had significant effect on the reaction rates and, for stable operation, maximum allowable stirring rate of 1500 rpm supplemented by an emulsifier concentration substantially higher than the critical micelle concentration (CMC, 8.1×10^{-3} M at 25°C [13]) was used.

In the presence of ammonia, it was found that the ligand to catalyst ratio of 3:1 is most favorable to promote the oxidative coupling reaction. Decreasing the ligand to catalyst ratio below 3:1 led to decreases in the reaction rates, since the amount of ligand become insufficient to pull the metal to the O–W interface where the reaction occurs. Increasing ligand to catalyst ratio also resulted in diminishing the reaction rate. Evidently, up to the ligand to catalyst ratio of 3:1, an increase in the ratio enhances complex formation and promotes the reaction, but above the ligand to catalyst ratio of 3:1, the excess ligand incrementally deprives the substrate, oligomer intermediates and oxygen access to the catalyst's coordination sites and the reaction is inhibited. With a suitable surface-active ligand such as *N,N*-dibutylethylenediamine (DBEDA), the reaction proceeded fast without any detectable induction period and PPO was preferentially produced via C–O coupling according to the stoichiometry as follows:



Provided that sufficient ammonia exists, no C–C coupling product of 2,6,2',6'-tetramethyl-1,4-diphenoquinone (see below for the stoichiometry) was detected over the ligand to catalyst ratio of 1:1 to 4:1 examined.



The characterization studies revealed that the oxidative coupling product showed good match with the PPO standard. The FT-IR spectra of the product isolated in the reaction mixture was consistent with the PPO standard, and the peak at 830 cm^{-1} which is known as the indicative of high molecular weight product [5] was clearly observed. In the ^1H NMR spectra, again almost identical spectra were obtained between the reaction products and the PPO standard, and the ratio of aromatic protons to methyl protons corresponds to 1:3 as expected in PPO. The absence of any other significant peaks indicates that no cross-linking or ring substitution was taken place, which supported that only linear polymer was formed with 2,6-dimethylphenylene oxide as the repeat unit.

The reaction rate increases significantly by the presence of NH_3 in the aqueous phase which functions as a deprotonating agent for 2,6-dimethylphenol. However, excess ammonia (> 0.25 M) caused inhibition effect probably by competing for the catalyst's coordination sites against the substrate and oxygen. The formation of polymer could be inferred from a visible viscosity increase of

the reaction mixture and also from a distinctive color development of the reaction mixture during a run. After the reaction condition was adequately met for the polymer formation, gradual change of color from bluish green initially to olive green was observed as the time elapses. Furthermore, in the presence of a suitable surface-active ligand, the olive green reaction mixture was spontaneously separated into three portions upon standing overnight after the reaction: a pale blue aqueous phase on top, a dark brown organic phase at the bottom, and a greenish interfacial emulsion layer.

3.2. Relative effectiveness of the surface-active ligands

The ligand screening results are shown in Fig. 1. Among the ligands tested, bidentate ligands such as substituted ethylenediamines were proven more effective than monodentate ligands to promote the oxidative coupling of 2,6-dimethylphenol. In particular, when DBEDA was used, the reaction rate was more than 10 times as fast as that with triethyl phosphite (TEP) or tributyl phosphite (TBP), and concurrently high PPO yield of close to 95% was obtained. Furthermore, except for *N,N'*-dimethylethylenediamine (DMEDA) which showed relatively long induction period of about 35 min, no apparent induction period was detected under the reaction conditions. For TEP or TBP, no reaction occurred in the absence of ammonia. The general effectiveness of substituted ethylenediamines as catalyst ligands may be ascribed to their ability to simultaneously bind onto the catalyst and deprotonate the substrate and the oligomer intermediates. The key to the preparation of an active coupling catalyst is the placement of coordinatively unsaturated metal centers in close proximity to one another. The desired proximity may be more easily attained by using a bidentate ligand which aids to form a binuclear complex with two metal ions, rather than chelate complexes with a single metal ion [14]. In the case of a monodentate ligand which attached to each single copper ion, the average distance between the adjacent copper neighbors is larger than the range of copper–copper separations in binuclear copper compounds [15–17]. A large separation between nearest copper centers, where phenoxy radicals are formed by a redox reaction between phenolate anions and the oxidized metal centers [14], is unfavorable to the oxidative coupling reaction of phenolic substrate.

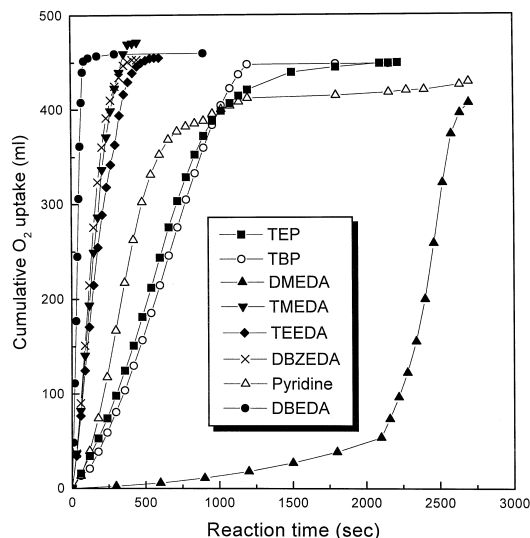


Fig. 1. Cumulative O₂ uptake profiles with different ligands.

The large variation in rate within the substituted ethylenediamine family suggests that other factors may also be involved. A consideration of the molecular structures of the ligands suggests that (1) the ligands may have varying ability to form a binuclear catalyst complex and (2) the catalyst complex may also have varying surface activity, which is closely related to its ability to draw the transition metal complex catalyst to the interfacial area. The fact that DBEDA gave the most active catalyst complex may be rationalized in terms of an optimal balance between binuclear complex formation and surface activity of the catalyst complex, and its ability to deprotonate the substrate and oligomer intermediates.

3.3. Comparison with homogeneous reaction mode

We examined briefly the differences between biphasic and homogeneous coupling polymerization reactions of 2,6-dimethylphenol. For this, it was established at the outset that those copper complexes formed with the ligand such as TBP, DBEDA, and pyridine are all very soluble in the chosen organic phase, chloroform, and consequently the reactions could run homogeneously. Copper complexes formed with TBP or DBEDA were also completely soluble in water, indicating the surface-active properties of these ligands. With addition of ammonia, however, the former complex in water formed a precipitate, whilst the latter formed a precipitate in chloroform. Copper complex formed with pyridine was readily soluble in chloroform, but precipitated out in water. With ammonia, both organic and water single phase produced a precipitate, whilst no precipitate was formed in the biphasic conditions of Table 1. The variations of the steady state oxygen uptake rates at different reaction modes are summarized in Table 2. In biphasic reactions, the distribution of copper in the reaction mixture was determined by measuring the metal concentrations in the aqueous phase, organic phase and interfacial emulsion layer after the completion of the phase separation. The results are summarized in Table 3. As will be shown shortly, it was found that the attribute of the ligand used and the presence of ammonia significantly affected the reaction rates as well as the average molecular weight of polymer product.

3.3.1. Cu–DBEDA complex catalyst system

Highest steady state oxygen uptake rate (4.73 M/h) was observed when DBEDA was used as a ligand in the presence of ammonia, and the reaction rates dropped to approximately to half (2.11 M/h) without ammonia. The reaction without ammonia progresses slower, since DBEDA should function not only as a ligand but as a deprotonating agent as well. Table 3 shows the distribution of copper in the biphasic reaction mode using Cu–DBEDA complex as a catalyst with or without ammonia present. In the absence of ammonia, highly segregated copper complexes could be isolated

Table 2
Steady-state oxygen uptake rates in biphasic and one phase modes

Ligand	O ₂ uptake rate (M/h)		
	Biphasic mode		One phase mode
	With NH ₃	Without NH ₃	
<i>N,N</i> -Dibutylethylenediamine	4.73	2.11	3.93 (0.32 ^a)
Tributyl phosphite	0.36	Negligible	Negligible (0.22 ^a)
Pyridine	0.61	0.01	0.83 (0.09 ^a)

^aOxygen uptake rate in the reaction with NH₃.

Table 3
Distribution of copper in the biphasic reaction mixture

Ligand	Condition	Phase	Copper distribution (%)
<i>N,N</i> -Dibutylethylenediamine	Without NH ₃	Organic phase	5.1
		Interfacial layer	88.9
		Aqueous phase	4
	With NH ₃	Organic phase	2.2
		Interfacial layer	75.6
		Aqueous phase	19.4
Tributyl phosphite	With NH ₃	Organic phase	27.4
		Interfacial layer	50.8
		Aqueous phase	20.2
Pyridine	Without NH ₃	Organic phase	66.6
		Interfacial layer	31.5
		Aqueous phase	0.6
	With NH ₃	Organic phase	0.5
		Interfacial layer	48
		Aqueous phase	48.2

at the interfacial area, and despite the slower reaction rates, it may be advantageous to run the biphasic reaction without ammonia to achieve enhanced catalyst separation. The presence of ammonia in the reaction mixture resulted in the increased concentration of copper species in aqueous phase. It can be presumed that a small portion of copper may be transferred to aqueous phase by coordination of ammonia, which preferentially dissolves in aqueous phase.

In one-phase (organic) mode, Cu–DBEDA complex produced relatively fast coupling reaction rate (3.93 M/h) aided by enhanced solubilities of the substrates and its oligomers, even though the reaction rate was not as fast as that in the biphasic reaction in which the reaction mostly occurs at the O–W interfacial area and ammonia in aqueous phase deprotonating the substrate. An addition of ammonia led to precipitate of Cu–DBEDA complex with bluish color. The precipitation resulted in a heterogeneous reaction medium, and hence decreases the frequency of encounter between the reactants, catalyst complex, and polymer chains. At the same time, competition of ammonia with ligand for catalyst's coordination sites increases, because of the absence of aqueous phase. The combined effect seriously reduced the coupling reaction rates.

An important difference between one-phase and biphasic reaction scheme was reflected in the total cumulative oxygen uptake volume consumed during the coupling reaction. As shown in Fig. 2, the total amount of oxygen uptake in biphasic reaction nearly met with the stoichiometric amount for PPO formation independent of the presence of ammonia. On the other hand, almost 30% excessive oxygen was additionally found consumed in one-phase reaction. The relatively low PPO yield in one-phase reaction (82%) in contrast to that in biphasic reaction (95%) makes it possible to presume that the surplus oxygen consumption is due to either the formation of side products or low molecular weight polymer.

3.3.2. Cu–TBP complex catalyst system

In the reaction catalyzed by Cu–TBP complex, the presence of ammonia was essential to run a reaction in both the biphasic and one-phase organic mode. However, those reaction rates obtained were far slower than with DBEDA. Cu–TBP complex dissolves very well in chloroform and water, but blackish precipitation would occur in water in the presence of ammonia. No precipitates, however, form in biphasic media even with ammonia. According to Table 3, only approximately 50% of the

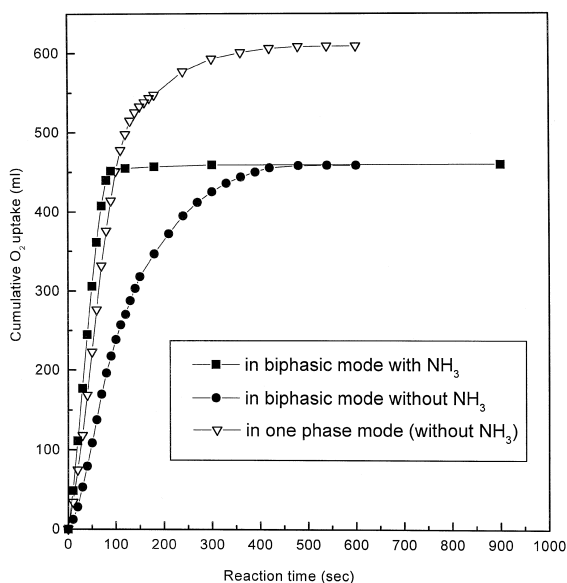


Fig. 2. Cumulative O₂ uptake profiles of the oxidative coupling of 2,6-dimethylphenol in biphasic and one phase modes.

total copper species could be isolated in the middle emulsion layer, and roughly the same portion of the rest is divided between organic and aqueous phases. It appears that copper exists mainly as Cu–NH₃ complex in aqueous phase and as Cu–TBP complex in organic phase, respectively; the UV-absorption peak at 273 nm for the aqueous phase complex was consistent with that of Cu–NH₃, while the UV-absorption peak of 255 nm for the organic phase matched well with that of Cu–TBP complex. The distribution of copper in the biphasic mixture indicates that TBP has lower surface-activity than DMEDA. It is believed that the lower surface-activity of Cu–TBP complex led to slower coupling reaction rates in biphasic reaction scheme.

In one-phase reaction mode with ammonia, though the reaction can be regarded as homogeneous, ammonia cannot effectively deprotonate the substrate and competes strongly for the catalyst's coordination sites due to the absence of aqueous phase. Consequently, it makes the reaction rate slower than that in the biphasic reaction.

3.3.3. Cu–pyridine complex catalyst system

Pyridine has been used as a ligand in conventional homogeneous PPO synthesis reaction. Cu–pyridine complex dissolves well in organic phase, and as Table 2 shows the reaction in one-phase mode is better to attain fast reaction rates than in biphasic mode. When the solvent was changed from chloroform to pyridine, further improvement in reaction rate to 2.01 M/h was obtained. However, bluish precipitate was formed if ammonia is present in one-phase reaction, and the reaction rate dropped sharply. Copper distribution in Table 3 indicates that pyridine indeed has a strong affinity for organic phase, and, in the absence of ammonia, Cu–pyridine complex preferentially dissolves in organic phase rather than aqueous phase in the biphasic media. On the other hand, the presence of ammonia leads to transfer of most copper species to aqueous phase. Thus, in biphasic mode, reaction rates are far slower than with DBEDA, since little interfacial reaction takes place. Higher reaction rates were observed with ammonia in biphasic medium due to its deprotonating activity.

3.4. Average molecular weight distribution and product selectivity

Since the coupling site on a growing polymer chain becomes increasingly difficult to reach as the number of chain segments that can obstruct it rises, a higher collision frequency and a shorter diffusion path length are important to the formation of high molecular weight product [18]. In biphasic reaction, fine emulsion that can hold more polymer chains in active suspension provides a large interfacial area and a shorter diffusion path length, thus, increases the frequency of encounter between the reactants, catalyst complex, and polymer chains. In this regard, biphasic reaction scheme is advantageous in attaining high molecular weight product. It is known that the molecular weight range of 25,000–60,000 is commercially useful [19].

The variations of the molecular weight with different reaction modes are shown in Fig. 3. In biphasic conditions, depending on the ligand used, widely different average molecular weights were obtained for the corresponding products, in the decreasing order of DBEDA (48,000, with NH_3) > DBEDA (36,000, without NH_3) \gg TBP (12,000) > pyridine (5000). The results manifest that biphasic reaction with an appropriate surface-active ligand such as DBEDA is more favorable for forming higher molecular weight polymer. The presence of ammonia also contributes to increases in the molecular weight of product via aiding deprotonations of the substrate and oligomers. When surface-active DBEDA is used without ammonia, though homogeneous reaction shows faster reaction rate than biphasic reaction, somewhat higher molecular weight product can be obtained in biphasic reaction. In the case of pyridine which has little surface-activity, homogeneous reaction scheme is suitable to accelerate the reaction rate as well as to obtain higher molecular weight product.

It is also of interest to note that the homogeneous counterparts of the oxidative coupling reaction [3–11] require the ligand to catalyst ratio to exceed 100:1 in order to promote the selective formation of PPO via C–O coupling. Formation of 2,6,2',6'-tetramethyl-1,4-diphenquinone side product via C–C coupling becomes progressively significant below the ligand to catalyst ratio of 100:1. By contrast, the biphasic coupling reaction produces PPO essentially quantitatively at a ligand to catalyst as low as 1:1.

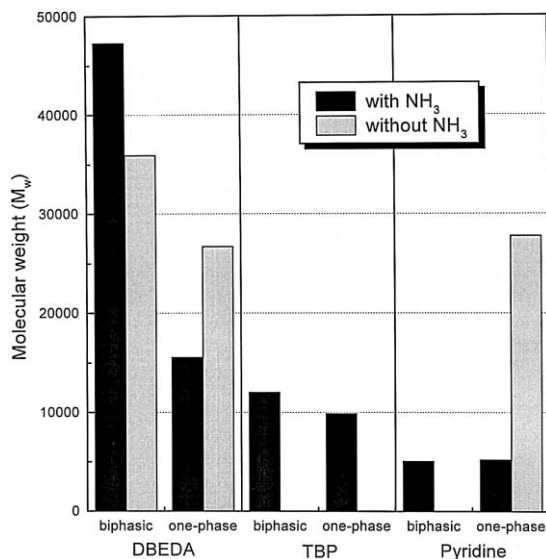


Fig. 3. Variation of the average molecular weight in different reaction media.

4. Conclusion

A biphasic reaction technique was applied to the synthesis of PPO in a chloroform–water biphasic mixture using a surface-active complexes copper as the coupling catalyst, ammonia as the base to deprotonate the 2,6-dimethylphenol substrate, and DSS as the emulsifier with vigorous stirring.

Bidentate ligands were superior to monodentate ligands in promoting the oxidative coupling possibly due to their higher surface-activity and ability to form a binuclear complex with two metal ions. Particularly, with surface-active DBEDA, both the highest reaction rate and a polymer product of $M_w = 48,000$ could be obtained with 95% yield.

The use of a surface-active ligand such as DBEDA in biphasic reaction was essential to obtain both faster reaction rate and higher molecular weight polymer product in comparison with homogeneous counterpart. Moreover, the phase separation induced by the surface-active ligand makes it possible to recover the catalyst complex in a relatively compact form.

Acknowledgements

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