

Synthesis and Characterization of Low-Molecular-Weight Poly(2,6-dimethyl-1,4-phenylene oxide) in Water

Lei Gui, Huan Wang, Baoqing Shentu, Zhixue Weng

State Key Lab of Chemical Engineering, Department of Chemical and biological Engineering, Zhejiang University, Hangzhou 310027, China

Correspondence to: B. Shentu (E-mail: shentu@zju.edu.cn)

ABSTRACT: Low-molecular-weight poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with unimodal polydispersity was synthesized by oxidative polymerization of 2,6-dimethylphenol in the presence of Cu-ethylene diamine tetraacetic acid catalyst in water. A series of low-molecular-weight PPO oligomers with M_n ranged from 360 to 3500 were obtained. It was found that the molecular weight and polydispersity were affected by reaction time, reaction temperature, and catalyst concentration. Based on the detector response-elution volume curve and the molecular weight from gel permeation chromatography, a possible molecular weight growth mechanism was proposed. The structure and properties of low-molecular-weight PPO oligomers were characterized by atomic absorption spectroscopy, differential scanning calorimetry, Ubbelohde viscometer, and nuclear magnetic resonance spectroscopy. Compared to the commercial low-molecular-weight PPO, PPO oligomers synthesized in water had a much lower residual copper content. The relationships between T_g and M_n at relatively low-molecular weight are in good agreement with the equation proposed by Fox and Loshack. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: glass transition; monomers; oligomers and telechelics; theory and modeling

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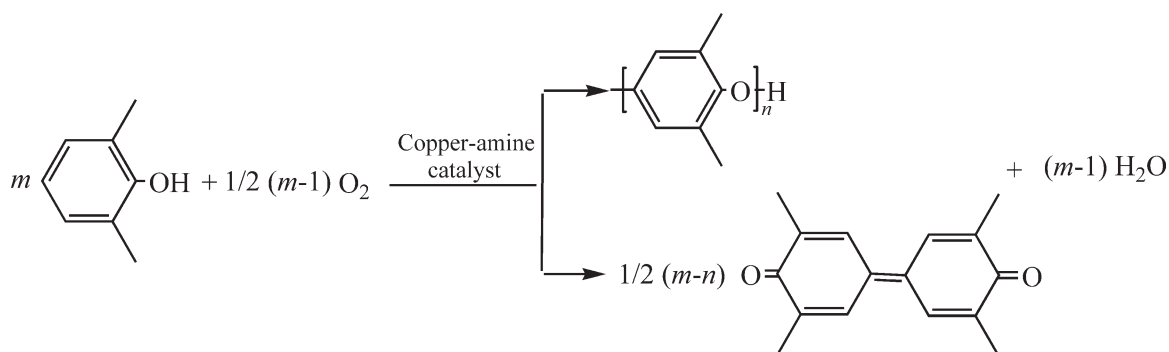
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INTRODUCTION

Oxidative polymerization of 2,6-dimethylphenol (DMP) catalyzed by copper-amine complexes^{1–3} provides a basic method to synthesize poly(2,6-dimethyl-1,4-phenylene oxide; PPO, Scheme 1). According to this method, PPO with high-molecular weight is obtained, which has excellent physical and electrical properties, such as good mechanical properties, high-dimensional stability, low-moisture uptake, high-thermal stability, low flammability, and low-dielectric constant.^{4–7} In view of these properties, PPO would be an excellent candidate material for electrical or electronic equipments, vehicle parts, business machines, adhesives, coatings, and composites. Besides, PPO is one of the potential materials to satisfy the demand for high-frequency substrates. However, high-molecular-weight PPO has some deficiencies, such as poor processability, high-melt viscosity, and low reactivity, when it is used as an additive for coatings and composites. For example, as a composite material for printed circuit board, PPO fails to blend with epoxy because of phase separation.⁸ The low-molecular-weight PPO could be a good solution to the problems mentioned earlier, while maintaining almost all the advantages. A great interest has been developed on a linear macromonomer or prepolymer with a number-average molecular weight of 1000–5000 over the past decades.

Low-molecular-weight PPO is generally prepared via redistribution or depolymerization of high-molecular-weight PPO with various phenolic derivatives in the presence or absence of radical initiators.^{9,10} The phenolic derivatives can be either DMP,¹¹ 3,3',5,5'-tetramethyl-4,4'-diphenoquinone (DPQ),¹¹ or tetramethyl bisphenol-A in the presence of dimethyl-aminopyridine.¹² However, the redistribution reaction of high-molecular-weight PPO often encounters problems, such as bimodal polydispersity, incorporation of radical initiators into polymer, and difficulty in controlling the exact molecular structure of PPO oligomer.⁸ Besides, most of the previous redistribution studies of PPO emphasized the understanding of the redistribution mechanism and the screening of potential initiators and phenols.^{13–18} Few researchers studied the molecular weight control of low-molecular-weight PPO.

In 2004, Nishide et al.¹⁹ first reported the polymerization of DMP in water using potassium ferricyanide as an oxidant to synthesize PPO, and then Nishide and coworkers^{20,21} have done some further research work on the oxidative polymerization of DMP in water. However, these previous works focus on the synthesis of high-molecular-weight PPO and look for the high-efficiency catalyst. As for the synthesis of the low-molecular-weight PPO oligomer in water, no report has been published so far.



Scheme 1. Oxidative polymerization of DMP.

Thus, the aim of our work is to overcome these deficiencies of redistribution and to develop a convenient method for the preparation of low-molecular-weight PPO with different specification of M_n and unimodal polydispersity in water. Water was used as reaction medium, copper-amine complexes as catalysts, and oxygen as an oxidant to achieve the oxidative polymerization of DMP. In this study, the influence of catalyst concentration, reaction temperature, and reaction time was investigated to synthesize low-molecular-weight PPO oligomer. The residual copper content, T_g , $[\eta]$, and phenolic end-group content of PPO oligomers with different molecular weight were investigated. The relationships between T_g , $[\eta]$ and M_n were also elucidated.

EXPERIMENTAL

Materials

Analytically pure DMP was purchased from Aldrich. Analytically pure copper dichloride (CuCl_2) and ethylene diamine tetraacetic acid (EDTA) were obtained from Shanghai Zhenxing Chemistry Co. and Sinopharm Chemical Reagent Co., respectively. Analytically pure sodium chloride (NaCl) and sodium hydroxide (NaOH) were supplied by Ningbo Chemistry Co. and Xiaoshan Chemistry Co., respectively. Chemically pure sodium *n*-dodecyl sulfate (SDS) was purchased from Shantou Chemistry Co. Low-molecular-weight PPO (SA 120[®]) was obtained from Sabc Basic. SA 120 has a number-average molecular weight of 2350 g mol^{-1} and polydispersity of 2.7.

Oxidative Polymerization of DMP in Water

A typical procedure for the oxidative polymerization of DMP in water catalyzed by Cu-EDTA complex is as follows: DMP (0.610 g, 5.0 mmol), NaOH (0.200 g, 5.0 mmol), and SDS (0.144 g, 0.5 mmol) were dissolved in water (90 mL). The aqueous solution (10 mL) of the complex of copper dichloride dehydrate (0.0086 g, 0.05 mmol) with EDTA (0.0226 g, 0.05 mmol) was added to the reactor, and the reaction mixture was vigorously stirred under oxygen at 50°C for 24 h. An off-white powder was obtained by filtration after salting out with NaCl in 88–92% yields.

To get the reaction time-course of molecular weight profile, a series of aliquots from the solution in specific reaction time, that is, 0.25, 0.5, 1, 2, and 4 h, were removed and then acidified, extracted with toluene, and sent to gel permeation chromatography (GPC) test immediately.

Characterizations

$^1\text{H-NMR}$ spectra were recorded by a GSX-270 spectrometer (400 MHz, JEOL Japan Electronics Co., Tokyo, Japan) in CDCl_3 with tetramethylsilane as an internal standard. δ (ppm): 7.07 (s, Ar-H of terminal PPO next to hydrogen group), 6.46 (s, Ar-H of internal PPO), 6.35 (s, Ar-H of terminal PPO next to hydroxy group), 4.28 (s, Ar-OH of terminal PPO), 2.15 (s, Ar- CH_3 of terminal PPO next to hydroxy group), and 2.07 (s, Ar- CH_3 of internal PPO). The phenolic end-group content was calculated from $^1\text{H-NMR}$ spectrum by the integral ratio of protons in methyl and phenol end group.

The intrinsic viscosity of PPO in toluene at 25°C was determined with an Ubbelohde viscometer (capillary diameter: 0.54 ± 0.01 mm, capillary length: 120 ± 3 mm).

The number-average molecular weight and polydispersity of PPO were determined by GPC (Waters 1525/2414, Waters Instruments, Milford, MA) equipped with Waters Styragel HT4/HT3/HR1 columns and a refractive-index detector at 30°C. The mobile phase was toluene and was maintained at a flow rate of 1.0 mL/min. The molecular weight was calibrated with polystyrene standards.

The glass transition temperature of PPO was measured with a Perkin-Elmer DSC7 apparatus, equipped with a PE7700 computer and TAS-7 software. Dried samples of 3–7 mg PPO were measured with a heating and cooling rate of 20°C/min. The samples were heated to 300°C, kept at that temperature for 2 min, cooled to 50°C, and reheated to 300°C. The glass transition temperature was determined in the second heating scan.

The content of side-product DPQ was measured by UV-vis spectrophotometer (Shanghai Xinyi Instrument Co., Shanghai, China) in 421 nm. The concentration of DPQ (c , mol L^{-1}) in toluene was calculated according to Beer-Lambert's law [eq. (1)].

$$A = \lg(I_0/I) = \epsilon cl \quad (1)$$

where I_0 is the incident light intensity, I is the transmitted light intensity, l is the thickness of the colorimetric utensil, and ϵ is the molar absorption coefficient of DPQ, which was determined to be 6.5×10^4 $\text{L mol}^{-1} \text{cm}^{-1}$ by Beer-Lambert's law.

The residual copper content in PPO without any copper removal was measured by atomic absorption spectroscopy (HITACHI 180-50, San Jose, CA) by dissolving of the polymer in 40% phenyl sulfonic acid.

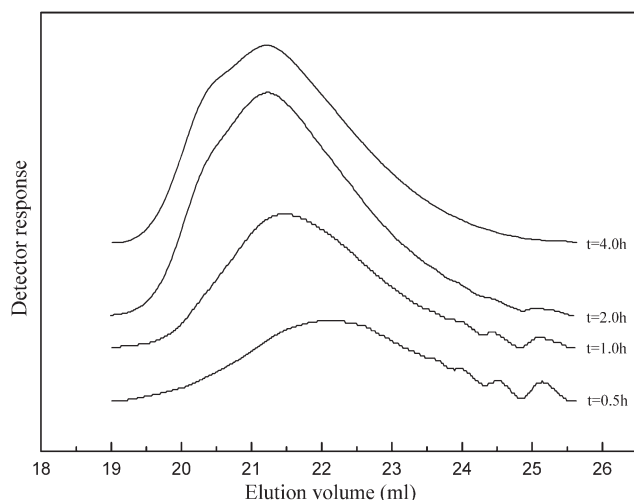


Figure 1. GPC traces of the low-molecular weight PPO oligomer formed in different reaction time: $t = 0.5$ h (entry 3, Table I); $t = 1.0$ h (entry 4, Table I); $t = 2.0$ h (entry 5, Table I); $t = 4.0$ h (entry 6, Table I). The polymerization was carried out with a copper catalyst concentration of $0.0005 \text{ mol L}^{-1}$ at 50°C .

RESULTS AND DISCUSSION

Influence of the Reaction Time on the Molecular Weight of PPO Oligomer

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) oligomer with a specific molecular weight could be formed through terminating the reaction at a specific time. This approach is difficult to achieve in the organic solution reaction for the extremely high-chain growth rate, where the molecular weight of formed PPO increased to thousands within a few minutes.^{1–3} Undoubtedly, it is difficult to get the needed low-molecular-weight PPO with specific M_n through traditional approach. This is the reason why the present low-molecular-weight PPO must be prepared through redistribution or decomposition. To investigate the influence of the reaction time on the M_n and polydispersity of the PPO oligomer in water, a series of aliquots in specific reaction time were removed and then acidified, extracted with toluene, and sent to GPC test immediately. Those procedures could give us a direct access to a series of dependable time-course data about the change of the molecular weight.

The detector response-elution volume curves from GPC, which represent reaction time of 0.5, 1, 2, and 4 h, respectively, are shown in Figure 1. The peaks with retention volumes between 23.5 and 25.5 mL corresponded to very low-molecular weight PPO oligomers, that is, monomer elutes at 25.2 mL and dimer elutes at 24.5 mL. As the reaction time extended from 0.5 to 4 h, the peaks corresponding to low-molecular weight PPO oligomers became smaller and smaller. No obvious peaks could be observed in this retention volume range when the reaction time was 4 h, while no apparent change can be seen in principal peak when the reaction time was more than 1 h. Although the reaction between low-molecular weight oligomers could not lead to a rapid increase of molecular weight, the polydispersity reduced obviously because of the disappearance of very low-molecular weight oligomers.

Table I. Influence of the Reaction Time on the Molecular Weight of PPO Oligomer^a

Entry	Reaction time (h)	M_n^b	Polydispersity ^b
1	0	122	–
2	0.25	360	4.50
3	0.5	630	3.92
4	1	960	3.07
5	2	1330	2.91
6	4	1660	2.57
7	6	1940	2.49
8	9	2530	2.35
9	12	2800	2.16
10	15	2910	2.07
11	18	3090	2.02
12	21	3310	2.05
13	24	3530	2.07

^aThe polymerizations were carried out in water under oxygen with copper catalyst of $0.0005 \text{ mol L}^{-1}$ at 50°C ; DMP of 0.05 mol L^{-1} , sodium hydroxide 0.05 mol L^{-1} , and sodium *n*-dodecyl sulfate 0.005 mol L^{-1} . All the aliquots were acidified, extracted with toluene, and sent to GPC test immediately, ^bDetermined by gel permeation chromatography relative to polystyrene standards in toluene.

The molecular weight data obtained from the detector response-elution volume curve are summarized in Table I, and the M_n -time curve is shown in Figure 2. The molecular weight increased dramatically with the reaction time at the initial stage, which is similar to the one in organic solution.²⁴ When the reaction time was 1 h, the M_n was 960, indicating that the polymerization degree (n) is 8. The chain length growth rate slowed down from this time. However, our former work²⁵ showed that PPO oligomer is insoluble even in alkaline water in 30°C when n is greater than 6. The value of n in our former work was determined by measuring the M_n when PPO oligomers have just precipitated from water to form latex particles, while the

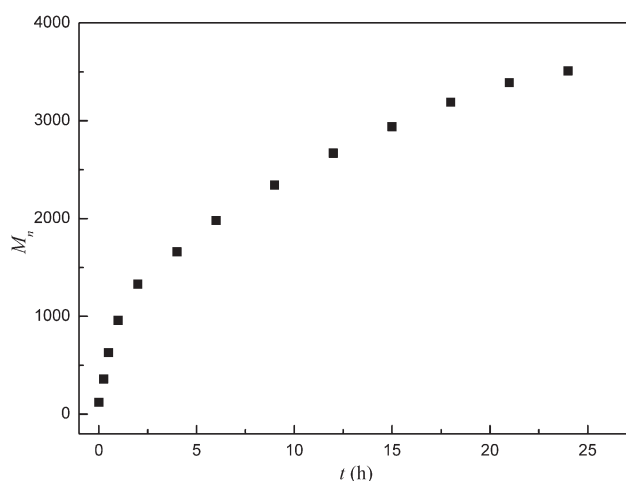


Figure 2. Relationship between the molecular weight and the reaction time (refer to Table I).

Table II. Influence of Reaction Temperature on the Oxidative Polymerization of DMP in Water^a

Entry	Temperature (°C)	PPO yield (%)	DPQ yield (%)	M_n	Polydispersity
1	50	92	0.20	2800	2.16
2	60	91	0.18	3200	2.45
3	70	90	0.19	3500	2.07
4	80	92	0.21	3800	2.20

^aAll the polymerizations were carried out in water under oxygen with copper catalyst of $0.0005 \text{ mol L}^{-1}$; reaction time of 12 h, DMP 0.05 mol L^{-1} , sodium hydroxide 0.05 mol L^{-1} , and sodium *n*-dodecyl sulfate 0.005 mol L^{-1} .

value of n in this work was determined from the trend of the M_n -time curve, and a little difference in the values of n may exist. On one hand, when PPO oligomers have just precipitated from water to form latex particles, their hydrophilicity is still strong and can swell in water, resulting in the relative high-polymerization rate and then the increase of the value of n . On the other hand, the PPO oligomers in this work were synthesized in high temperature than that in our former work, and the high temperature would lead to the high solubility of PPO oligomers in water, which also results in the high-polymerization rate and then the increase of the value of n . Therefore, when n is greater than 8 in this study, the reactivity of PPO oligomers decreases, and then the chain-length growth rate slowed down.

Influence of the Reaction Temperature on the Molecular Weight of PPO Oligomer

Table II shows the effect of the reaction temperature on the oxidative polymerization of DMP in water. In the oxidative polymerization of DMP in organic solvent, the high-reaction temperature above 50°C will lead to the high content of DPQ.²² Blais and Manley²² suggested that this behavior may be due to the presence of at least two catalytic species, one of which favors C—O coupling and the other C—C coupling. Then, Hay²³ reported that as the temperature of the reaction mixture rose, polymers with high-molecular weight were readily obtained with only small amounts of the DPQ as a by-product, when bidentate amines were used as ligands.

In the oxidative polymerization of DMP in water with EDTA used as bidentate ligand, the by-product DPQ content remained at a very low level, and no significant change occurred with the increment of reaction temperature. And this DPQ content is much lower than the product obtained in organic solution ($>1\%$).²⁴ Meanwhile, the molecular weight of PPO apparently increased with the increase in temperature. This phenomenon may be due to the following two reasons. First, at high temperature, the low-molecular weight oligomer with somewhat higher n could also be dissolved in the water,²⁵ resulting in the further oxidative polymerization and the increase in the molecular weight before forming latex particles. Second, the high temperature will enhance the activity of the polymer chain and increase the mutual collision probability between the chains, thereby increase the molecular weight of product formed.

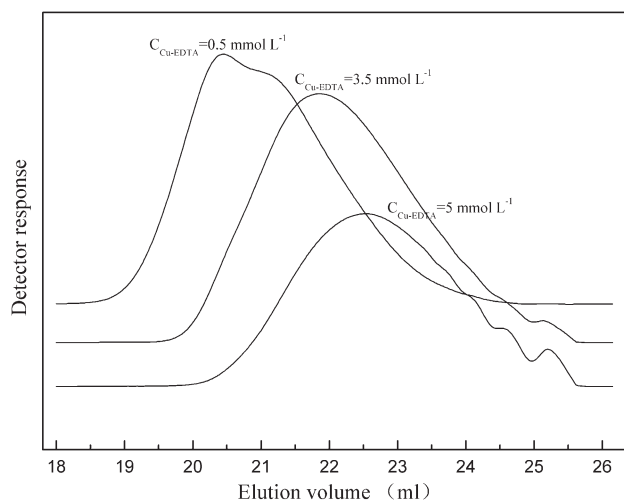


Figure 3. GPC traces of low-molecular-weight PPO formed in different catalyst concentrations: 0.5 mmol L^{-1} (entry 8, Table III); 3.5 mmol L^{-1} (entry 3, Table III); 5 mmol L^{-1} (entry 1, Table III). All the polymerizations were carried out at 50°C , and reaction time was 24 h.

Influence of the Catalyst Concentration on the Molecular Weight of PPO Oligomer

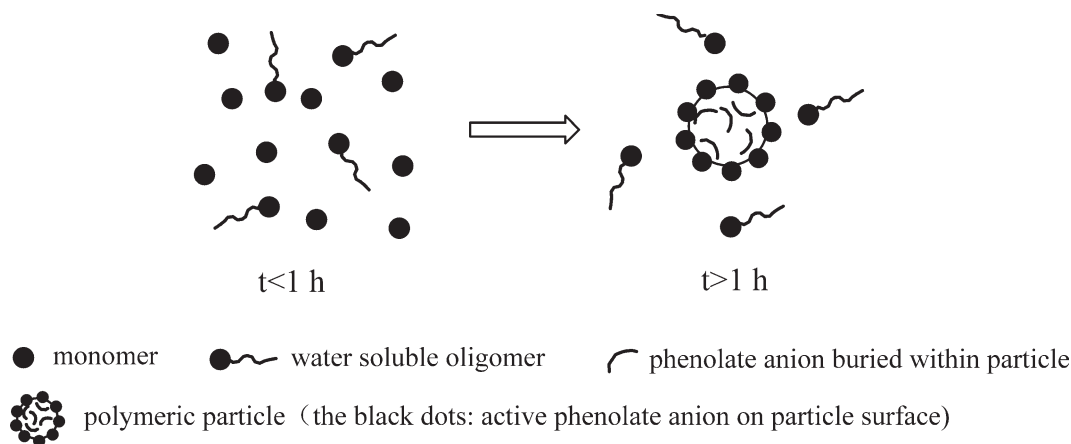
The amount of Cu-EDTA is a key factor in affecting the M_n and polydispersity of the resulting PPO oligomer. The effect of Cu-EDTA content on the M_n and polydispersity was investigated. The typical detector response-elution volume curves from GPC, which represent catalyst concentration of 0.5 , 3.5 , and 5 mmol L^{-1} , respectively, are shown in Figure 3. In the condition of high-catalyst concentration, the peaks of monomer and dimer are obvious. However, when catalyst concentration drops to 0.5 mmol L^{-1} , the peaks of low-molecular weight oligomers disappear.

The molecular weight data obtained from the detector response-elution volume curves are summarized in Table III. The M_n increased with the decrement of Cu-EDTA concentration, while the polydispersity decreased. When the Cu-EDTA

Table III. Influence of the Catalyst Concentration on the Oxidative Polymerization of DMP in Water^a

Entry	[Cu-EDTA] (mmol L^{-1})	PPO yield (%)	M_n	Polydispersity	Residual Cu content ^b (ppm)
1	5.00	87	360	4.52	0.9
2	4.00	89	740	3.36	1.0
3	3.50	89	1100	2.80	1.1
4	3.00	91	1300	2.54	0.9
5	2.50	90	1900	2.49	1.0
6	2.00	92	2200	2.18	1.0
7	1.25	92	3000	2.18	1.1
8	0.50	91	3500	2.07	1.2

^aAll the polymerizations were carried out in water under oxygen at 50°C ; reaction time of 24 h, DMP 0.05 mol L^{-1} , sodium hydroxide 0.05 mol L^{-1} , and sodium *n*-dodecyl sulfate 0.005 mol L^{-1} . ^bMeasured by atomic absorption spectroscopy by dissolution of the polymer in 40% phenyl sulfonic acid.



Scheme 2. The possible chain length growth mechanism of PPO oligomer formed in water.

concentration was 5 mmol L^{-1} (entry 1), the M_n of PPO oligomer was only 360 while the polydispersity was up to 4.52. The obvious peaks in 24.5 and 25.5 mL in the detector response-elution volume curve indicated that there are substantial PPO oligomers with very low-molecular weight. As the catalyst concentration decreased to 3.5 mmol L^{-1} (entry 3), the M_n of PPO increased to 1100 while the polydispersity fell to 3.36. The peaks of very low-molecular weight oligomers become less obvious. When the catalyst concentration further reduced to 0.5 mmol L^{-1} (entry 8), the M_n of PPO rose to 3500, and the polydispersity fell to 2.07. The corresponding detector response-elution volume curve was a smooth one, indicating that PPO oligomer with narrow polydispersity was obtained, and the amount of very low-molecular weight oligomer was negligible.

In the oxidative polymerization of DMP in organic solvent, higher concentration of catalyst results in higher molecular weight of PPO. Endres et al.²⁴ suggested that higher catalyst concentration leads to increased overall rates and favors C—O coupling at a fixed ligand ratio. However, the polymerization of DMP in water is different to the one in organic solvent, because polymer chains may precipitate in water medium. The high-catalyst concentration will lead to generate a lot of low-molecular weight PPO oligomers in a short time and then form a lot of latex particles, which are unfavorable to the further oxidative polymerization.²⁵

The residual copper contents of PPO oligomers obtained under different catalyst concentration are also listed in Table III. Comparing with the SA 120[®] (residual copper: 120 ppm) that is obtained from organic solvent by redistribution, the residual copper content in PPO oligomer obtained from water is much low. Furthermore, catalyst concentration has no significant influence on the residual copper content. The high-residual copper content is detrimental to PPO when used in the field of insulating materials. The results indicate that water medium is more suitable for the preparation of the low-molecular-weight PPO with low-residual copper content, because the copper complex catalyst dissolves in water medium while previous organic medium traps the copper inside the polymer during precipitation.²⁰

Possible Mechanism of Molecular Weight Growth

On the basis of the experimental results, the possible mechanism for chain length evolution is shown in Scheme 2. In the initial

stage, when the reaction time (t) is less than 1 h (according to Figures 1 and 2), there are two types of phenolate anion in the reaction system, that is, monomeric phenolate anion ($n = 1$) and water-soluble oligomeric phenolate anion ($1 < n < 6$). Monomers react to form water-soluble oligomer rapidly in this stage.^{25–27} When t is more than 1 h, it comes the next reaction stage, during which most of the low-molecular weight oligomers ($n > 6$) cannot dissolve in water any more, and thus the polymeric particles are formed. The oligomers located on the surface of polymeric particles are active and can participate in the next coupling reaction, while the other oligomers buried within the particles lose their opportunity of further molecular weight growth.²⁵ In this stage, the reaction between water-soluble oligomers and active oligomers on particle surface makes a dominant contribution to the molecular weight growth and the decrease in polydispersity. As a proof to it, the peaks corresponding to low-molecular weight oligomers disappear gradually in Figure 1. As a result, water-soluble oligomers and active oligomers located on particle surface disappeared gradually.

T_g and Inherent Viscosity

There are some equations to predict the dependence of the glass transition temperature (T_g) on the molecular weight, and the most commonly used is Fox and Flory equation²⁸ [eq. (2)]

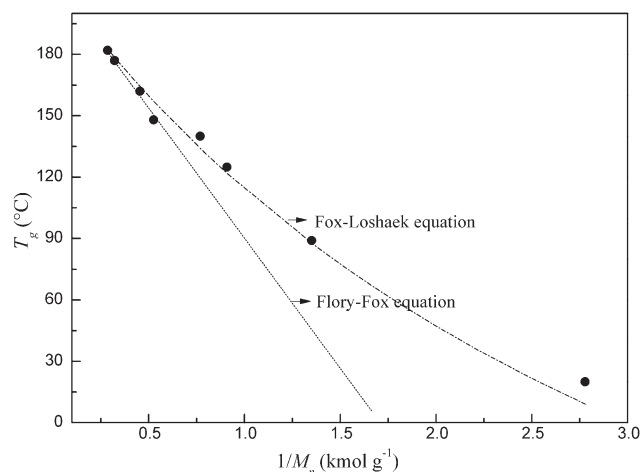


Figure 4. T_g as function of $1/M_n$ (●) T_g measured by DSC.

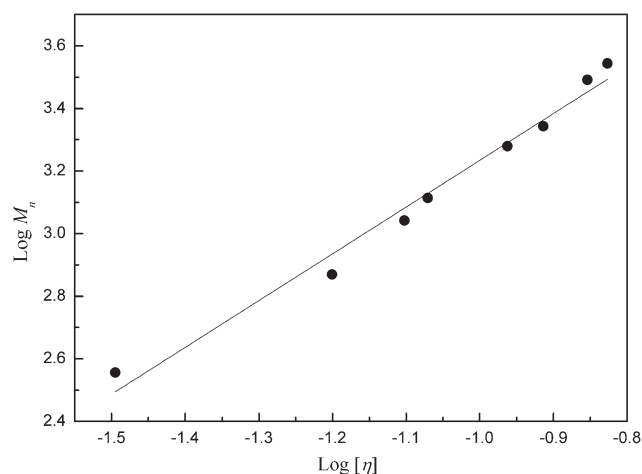


Figure 5. Log M_n as function of log $[\eta]$.

$$T_g = T_{g,\infty} - \frac{K}{M_n} \quad (2)$$

Here, T_g represents the glass transition temperature of a polymer with M_n (in K), $T_{g,\infty}$ is the T_g of a polymer of infinite chain length (PPO: $T_{g,\infty} = 490$ K), and K is the constant related to the volume of chain ends (PPO: $K = 12.73 \times 10^4$ g K mol $^{-1}$).²⁹

The T_g as measured by DSC is plotted as a function of $1/M_n$ for PPO oligomer in Figure 4, and the calculated T_g dependence on molecular weight according to Fox and Flory is given in Figure 4 as well. It was found that the T_g decreases with a decrease in the molecular weight. When the T_g of PPO oligomer measured is compared to that calculated according to eq. (2), a good agreement for the high-molecular weight PPO oligomer could be seen (above 1900 g mol $^{-1}$), while for low-molecular weight PPO oligomer, there is some deviation. It could be ascribed that at low-molecular weight, the “excess free volumes” of the chain ends are overlapping (K smaller).³⁰ As a result, the polymer chains are more stiff than predicted with eq. (2), and the glass transition temperature is higher. Considering this problem, the Fox–Loshack equation [eq. (3)] was introduced to plot the dependence of T_g on the molecular weight.³¹

$$T_g = T_{g,\infty} - \frac{K}{M_n + \frac{K}{T_{g,\infty}}} \quad (3)$$

The calculated T_g dependence on the molecular weight according to Fox–Loshack equation is given in Figure 4, too. Comparing the T_g of PPO oligomer measured with that calculated according to eq. (3), we can see a good agreement in almost the whole range except for an acceptable deviation in 360 g mol $^{-1}$. The $K/T_{g,\infty}$ value (PPO: 260) is unnegligible when M_n is low, which can neutralize the effect of the decrement of K . Therefore, this equation is more suitable to predict T_g in relatively low-molecular weight range especially under 1900 g mol $^{-1}$.

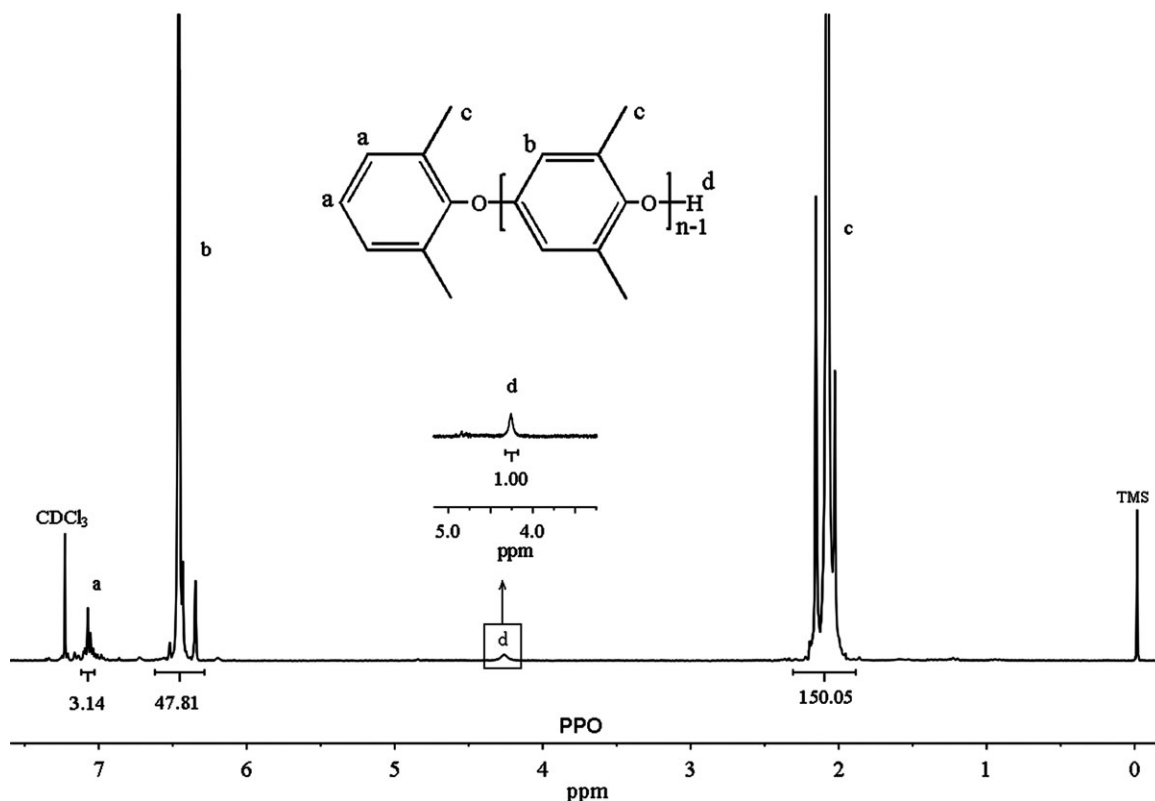


Figure 6. $^1\text{H-NMR}$ spectrum (400 MHz) of the low-molecular-weight PPO (Entry 7, Table IV), assignments of chemical shifts δ (in ppm): (a) 7.07; (b) 6.46; (c) 2.07; (d) 4.28.

Table IV. Phenolic End-Group Content and Functionality of PPO Oligomer

Entry	M_n	Phenolic end-group content ^a (mmol g ⁻¹)	Functionality
1	360	2.55	0.92
2	740	1.27	0.942
3	1100	0.881	0.97
4	1300	0.748	0.97
5	1900	0.511	0.97
6	2200	0.449	0.99
7	3000	0.333	1.00
8	3500	0.290	1.01

^aCalculated from the peak area ratio of $-OH$ and $-CH_3$ in 1H -NMR spectra in $CDCl_3$.

The intrinsic viscosity ($[\eta]$) of PPO oligomer was measured, and it was found that the intrinsic viscosity increases with increasing the molecular weight. According to Fox and Flory's theory,³² $\log M_n$ is plotted as a function of the measured $\log [\eta]$ (Figure 5). An approximate linear $\log M_n - \log [\eta]$ relationship with a slope of 1.50 and intercept of 4.75 could be seen. Therefore, at the range of low-molecular weight, the relationship between $\log M_n$ and $\log [\eta]$ for PPO oligomer is obtained [eq. (4)]. To examine the accuracy of eq. (4), we calculate the M_n of SA 120[®] ($M_n = 2350$, $[\eta] = 0.12$ dL g⁻¹) from its $[\eta]$. The calculated M_n is 2280, which is very close to the nominal value of 2350.

$$\log M_n = 1.50 \log [\eta] + 4.75 \quad (4)$$

Phenolic End-Group

The phenolic end-group content was calculated according to 1H -NMR spectrum using the integral ratio of protons in methyl and phenol end-group. A typical 1H -NMR spectrum and peak integral was shown in Figure 6. The high concentration of phenolic end-group means the high activity for further reaction when used as additive or reactant. Especially in the field of epoxy-modified PPO, high content of phenolic end-group has obvious advantages.

According to the M_n , theoretical phenolic end-group content can be obtained. Divided this theoretical value by the 1H -NMR calculated one, the functionality of product was obtained, and the results were shown in Table IV. It is apparent that the functionality is lower than 1, especially in the low-molecular weight range. It seems that the oxidation of phenolic end-group of the low-molecular weight PPO oligomer in the reaction process is responsible for the deviation.

CONCLUSIONS

Low-molecular-weight PPO with good processability and reactivity has attracted much attention for the potentials in the fields of printed circuit board, additives, and composites. In this study, we have developed a convenient and green method to synthesize PPO oligomers with different specification of

molecular weight, unimodal, and relatively low polydispersity. The decrease of the catalyst concentration or increase of reaction time and reaction temperature would lead to the increase in molecular weight of PPO oligomer.

Characterization results of various molecular weight PPO oligomers indicate that the residual copper content is much lower than that of commercial one due to the high solubility of copper complex catalyst in water. The relationships between T_g and M_n , $[\eta]$ and M_n are in accordance with the equations proposed by Flory and Fox. The functionality of PPO oligomer is lower than 1, and the oxidation of phenolic end-group may be the principal reason.

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