

Synthesis and Characterization of Aminated Poly(2,6-dimethyl-1,4-phenylene oxide)

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SYNOPSIS

In this article, the chemical modification of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was carried out by incorporating an amine group into the PPO backbone. A maximum monosubstitution degree of 65 mol % was reached. The effects of reaction conditions on the functional group content in PPO is discussed. The aminated PPO obtained was characterized by FTIR, ¹H-NMR spectroscopy, nitrogen analysis, DSC, solubility test, and X-ray diffraction studies. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), belonging to the class of thermally stable engineering plastics characterized by a high glass transition temperature ($T_g = 212^\circ\text{C}$) and good thermal stability under nonoxidizing conditions,¹⁻⁴ is one of the most widely used engineering plastics. Over the past few decades, to obtain special properties, much has been done on the modification of PPO such as bromination,⁵⁻⁷ phosphorylation,⁶⁻⁸ vinylation,⁹ carboxylation,^{10,11} amidation,¹² and Friedel-Crafts reactions¹³ such as acylation and sulfonylation.

We report herein the modification of PPO by incorporation of an amino group on the PPO aromatic unit, because the amino group, having a pair of electrons on a nitrogen atom and being an electron donor, is a basic group. The aim of these investigations was to prepare a new PPO matrix functional polymer, which not only maintains the excellent mechanical properties of the parent PPO, but also greatly enhances the compatibility with other polar polymers such as nylon and polycarbonate. It may thus be utilized as a functional material to create many new engineering plastic alloys. Further, these modified PPO are interesting in their own right since

they can be used as membrane materials for gas separation.

EXPERIMENTAL

Materials

Poly(2,6-dimethyl 1,4-phenylene oxide) (PPO), whose intrinsic viscosity was 0.58 dL/g (CHCl_3 , 25°C), was obtained from the Beijing Institute of Chemical Engineering. AR-grade sulfuric acid (98%), nitric acid (65%), hydrochloric acid (36%), acetic acid, NaI, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, etc., was obtained from the Guangzhou Chemical Reagent Factory. All these reagents and solvents were used as received.

Synthesis Procedure

There were two steps in synthesizing the aminated PPO ($\text{NH}_2\text{-PPO}$):

The first was the synthesis of nitrated PPO ($\text{NO}_2\text{-PPO}$). A certain ratio (v/v) of a mixed acid of nitric acid and sulfuric acid (sulfuric acid is a catalyst) was gradually added to a 5% (w/v) solution of PPO in CHCl_3 , reacting at room temperature for a period with stirring. At the end of the reaction, the resultant mixture was washed with distilled water until acid free. The separated polymer solution was precipitated in methanol, filtered off, and dried in vacuum at 60°C over 24 h.

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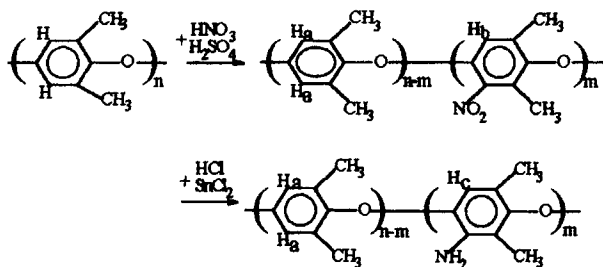


Figure 1 Reaction scheme with assignment of hydrogen.

The second step was reducing the nitrated PPO into aminated PPO. A mixture of 6.0 g dried nitrated PPO and 100 mL CHCl_3 was placed in 500 mL round flask fixed with a mechanical stirrer, a nitrogen gas inlet, and a reflux condenser. Seventy grams $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 2 g NaI were dissolved in a 150 mL mixed acid solution of hydrochloric acid and acetic acid (2 : 1), then added into the solution of nitrated PPO and refluxed under nitrogen at 60°C for 3 h. Since the aminated PPO was no longer soluble in CHCl_3 when the monosubstitution degree exceeded 15 mol %, methanol must be added in the reaction solution to prevent the precipitation of the aminated PPO when preparing a high monosubstitution degree NH_2 -PPO.

Measurements

The FTIR spectra were recorded from KBr pellets on an Analect RFX-65A spectrophotometer. The $^1\text{H-NMR}$ spectra were recorded from a Bruker 400 Mhz NMR spectrometer. PPO or NO_2 -PPO was dissolved in CDCl_3 , and NH_2 -PPO was dissolved in

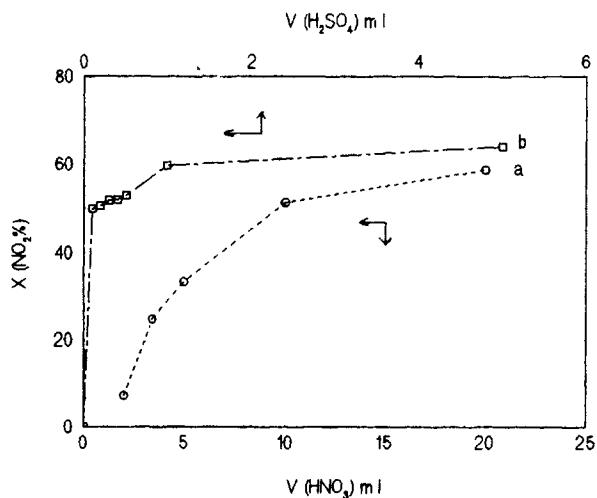


Figure 2 Effects of amounts on nitrification degree in PPO.

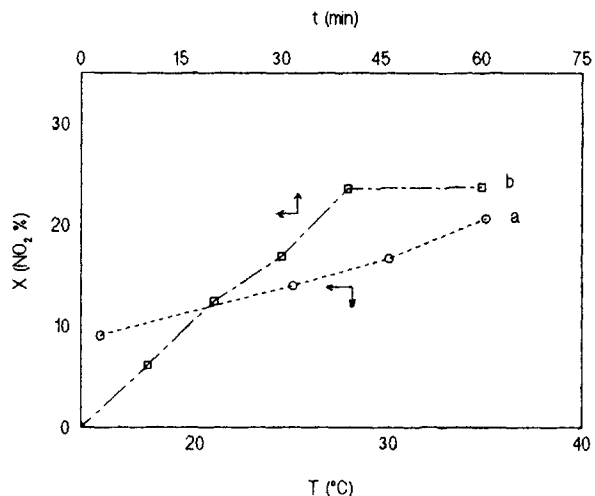


Figure 3 Effects of reaction time or temperature on nitrification degree on PPO.

a mixed solvent of a certain ratio of CDCl_3 and DMSO, scanning 32 times. The percent nitrogen was estimated by a Heraeus elemental analyzer CHN-O-RAPID. The X-ray diffractograms were obtained by a Rigaku Rint D/max-1200 X-ray diffractometer. Target: Cu; scan axis: $2\theta/\theta$, $2\theta = 4^\circ \sim 40^\circ$; wavelength: 1.5405×10^{-10} m.

DSC measurements were carried out with a Perkin-Elmer DSC-2C. The heating rate was $20^\circ\text{C}/\text{min}$ under N_2 atmosphere in all cases. The temperature range scanned was from 400 to 630 K. The samples weighed about 10 mg. T_g values were obtained at half the stepchange in C_p .

RESULTS AND DISCUSSION

This modification leads to a series of random copolymers as shown in the reaction scheme in Figure 1. When PPO is nitrated, the amounts of sulfuric acid or nitric acid, reaction time, and reaction temperature will affect the nitrification degree as shown in Figures 2 and 3. In general, the amounts of nitric acid are the most remarkable factor. Table I presents the experimental conditions of Figures 2 and 3, where $X(\text{NO}_2 - \%)$ = the molar monosubstitution degree of the nitro group in PPO aromatic units. We can get NH_2 -PPO with the desired monosubstitution degree by controlling the nitrification degree.

Since there was no good solvent to be found to dissolve the NO_2 -PPO when the monosubstitution degree of the nitro group in PPO aromatic units exceeded 70 mol %, the monosubstitution degree of

Table I Experimental Conditions of Figures 2 and 3

	PPO (g)	H ₂ SO ₄ (mL)	HNO ₃ (mL)	Time (min)	Temp (°C)
Figure 2(b)	5	Variable	10	30	30
Figure 2(a)	5	0.1	Variable	30	30
Figure 3(b)	20	0.3	10	Variable	30
Figure 3(a)	20	0.3	10	30	Variable

the aminated PPO obtained here was limited below 65 mol %. In this article, in all cases, XY-PPO represents that the monosubstitution degree of the Y group in PPO aromatic units is X mol %.

Typical ¹H-NMR spectra of the PPO, NO₂-PPO, and NH₂-PPO polymers are presented in Figure 4 together with the assignment of their proton resonances. Multiple resonances for the methyl groups of the modified polymers should be due to the sequence distribution of the structural units and it is difficult to provide an exact assignment at this time. The proton in N—H could not be assigned since it was merging with water proton resonances, which came from the DMSO solvent.

In all cases, the molar degree of monosubstitution of PPO aromatic units was determined from the ratio of integrals of proton resonances due to unsubstituted phenylenic units (signal H_a) and substituted

units (signal H_b or H_c). The following relationship has been used to calculate the molar degree of monosubstitution (represented by X) of the modified polymer:

$$X = I / (0.5I + I_a)$$

where I_a and I represent the integrals of protons designated as H_a and H_b (or H_c) in Figure 4, respectively.

The molar monosubstitution degree X was also calculated from the percent nitrogen, by using the following equation:

$$14X / (120 + XM) = Y / 100$$

where M = molecular weight of substituting group (NO₂— or NH₂—) and Y = percent nitrogen es-

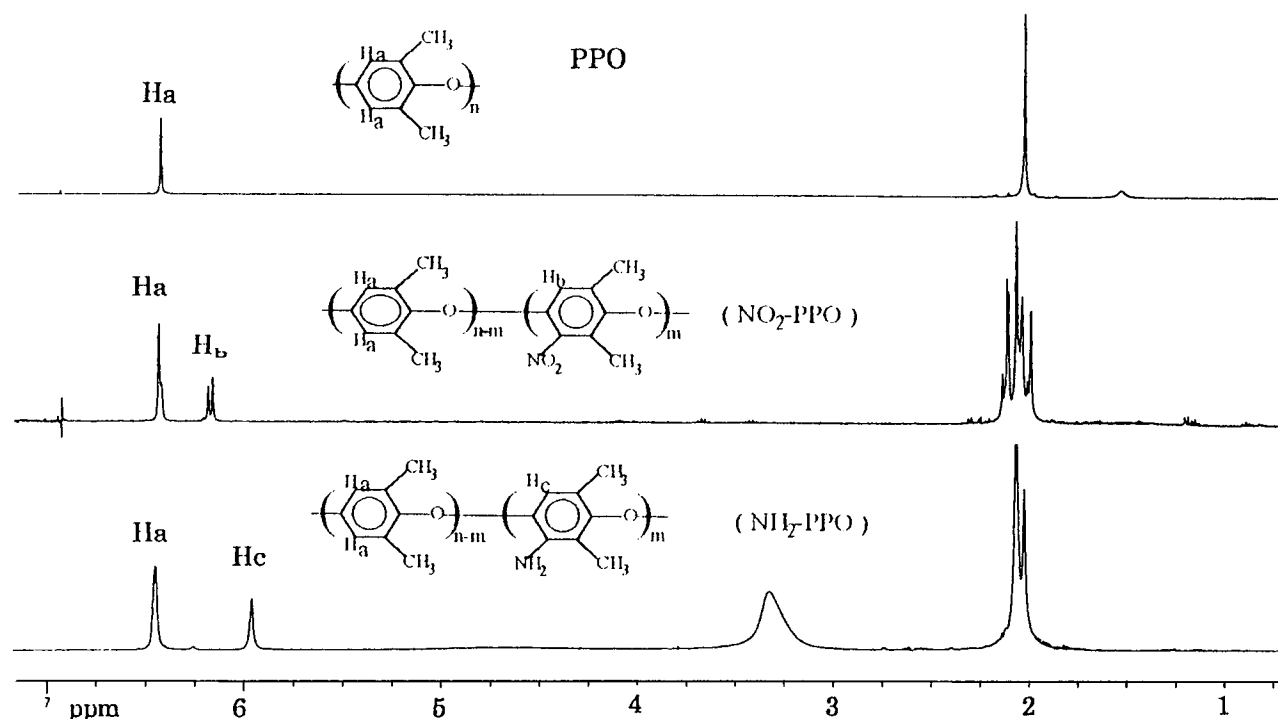
**Figure 4** ¹H-NMR spectra of the PPO, NO₂-PPO, and NH₂-PPO.

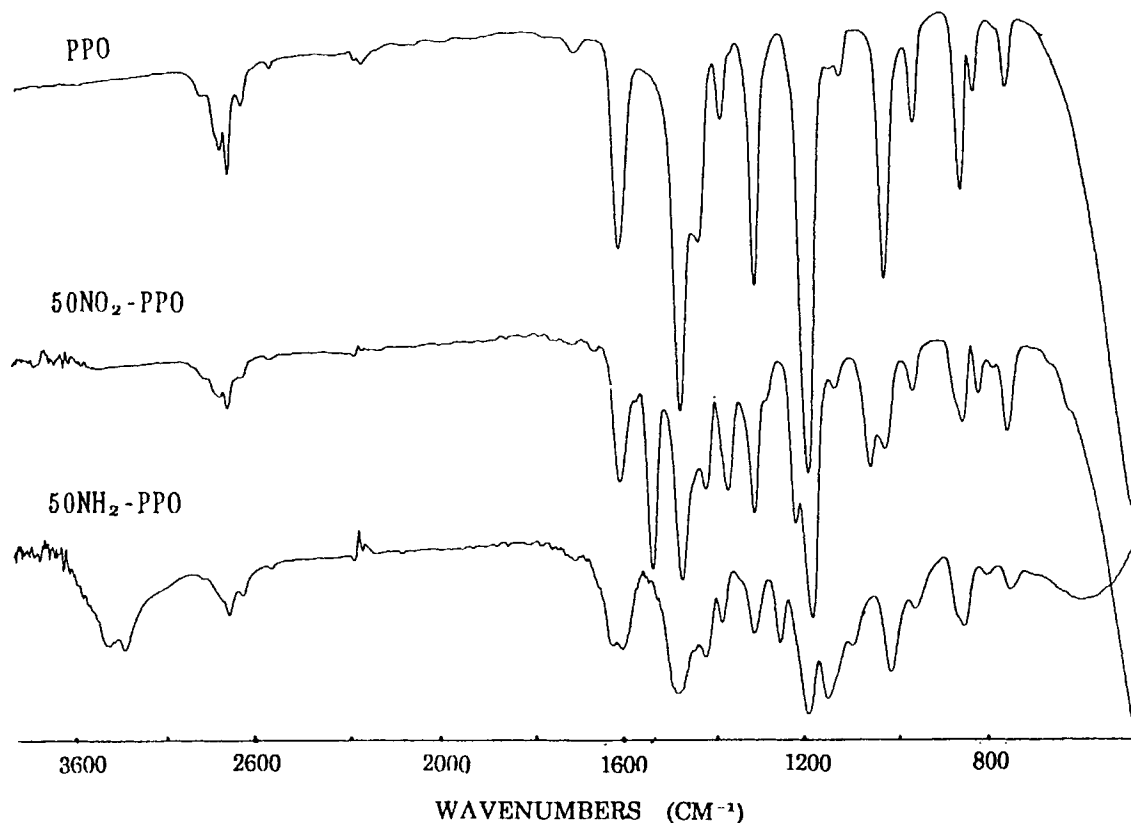
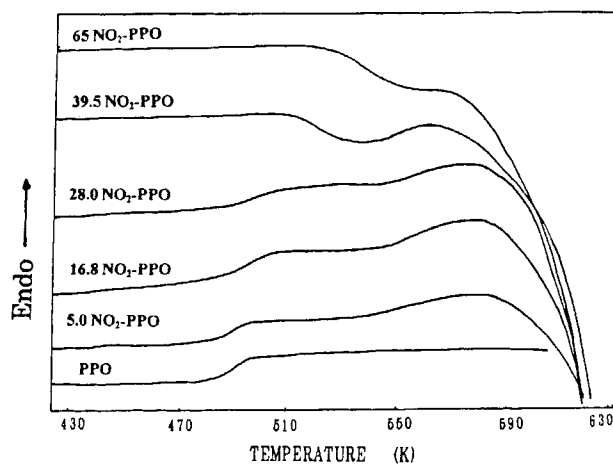
Table II Comparison of X_1 and X_2

Polymer	Nitrogen (%)	X_1 (%)	X_2 (%)
NH ₂ -PPO 1	3.05	31	36
NH ₂ -PPO 2	3.36	40	43
NH ₂ -PPO 3	4.00	49	51
NH ₂ -PPO 4	4.17	52	54
NH ₂ -PPO 5	4.89	64	65

Where X_1 = molar monosubstitution degree determined by H-NMR and X_2 = molar monosubstitution degree determined by percent nitrogen.

timated. The molar monosubstitution degree obtained by ¹H-NMR and from percent nitrogen is in good agreement as shown in Table II.

Figure 5 represents some typical FTIR spectra of PPO, NO₂-PPO, and NH₂-PPO, which supported the ¹H-NMR results by demonstrating the presence of the NO₂— absorption at 1535 and 1365 cm⁻¹ in the nitrated PPO, and the attachment of pendent NH₂— in the aminated PPO was confirmed by the presence of bands at 3380 and 3440 cm⁻¹ due to N—H stretching and at 1627 cm⁻¹ due to N—H bending vibrations.

**Figure 5** FTIR spectra of the PPO, NO₂-PPO, and NH₂-PPO.**Figure 6** DSC curves of NO₂-PPO samples with various nitrification degree.

DSC results for nitrated PPO and aminated PPO are displayed in Figures 6 and 7. In this study, a series of nitrated PPO with a range of 5.0–65 mol % nitro group was studied as shown in Figure 6. When the monosubstitution degree did not exceed 28 mol %, there were two glass transitions. When this limit was exceeded, there was only a single exo-

thermic peak. It is suggested that the phenomenon was a consequence of the presence of a polar group aggregation domain which impeded the local chain segment movement, so there was another higher T_g besides a T_g mainly due to PPO. But in highly nitrated samples, where the concentration of the nitro group was above 28 mol %, as temperature was increased, there appeared only an exothermic peak. Maybe this is due to crosslinking which impedes all the chain segment movement.

A series of aminated PPO with a range of 6.0–6.5 mol % amino group was studied as shown in Figure 7, in which no T_g was observed; there was only a broad endothermic peak. This may be caused by intermolecular association which impeded the chain segment movement, and as temperature was increased, the dissociation of orderly intermolecular association took place gradually, so there was a broad endothermic peak.

Solubility tests showed that unlike the parent PPO the aminated PPO tended to be soluble in dipolar aprotic solvents with an increasing molar monosubstitution degree of the amino group; when the substitution exceeded 50 mol %, the aminated PPO was soluble in DMSO, DMF, DMA, and methanol, ethanol, etc., but was not soluble in nondipolar solvents such as CHCl_3 and toluene.

Powder X-ray diffraction studies shown in Figure 8 indicated that the parent PPO exhibited a pattern for a typical semicrystalline polymer; on the other hand, NO_2 -PPO and NH_2 -PPO showed the pattern typical of amorphous materials.

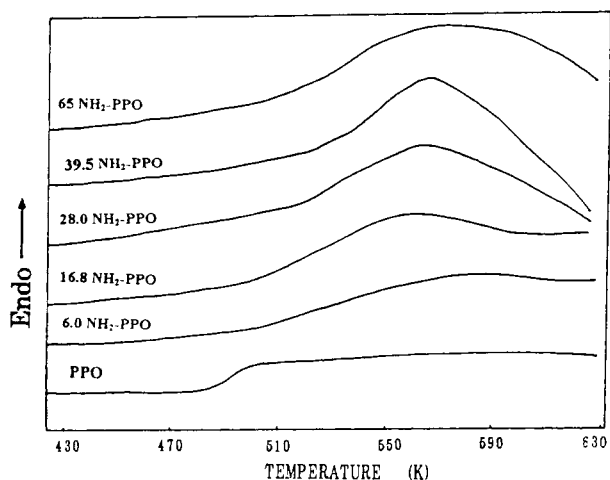


Figure 7 DSC curves of NH_2 -PPO samples with various amination degree.

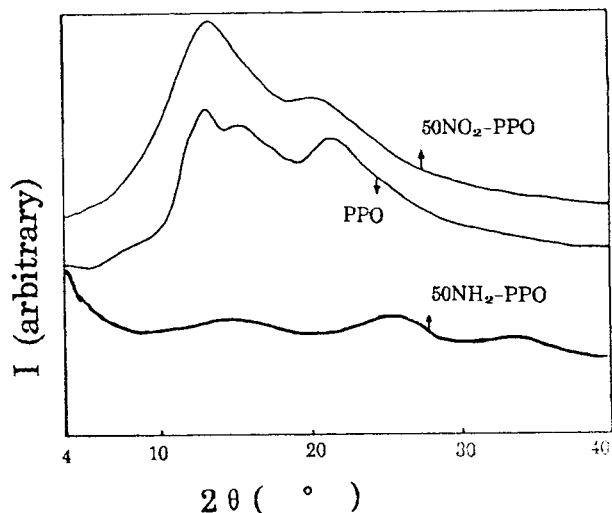


Figure 8 X-ray diffractograms of PPO, NO_2 -PPO, and NH_2 -PPO.

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REFERENCES

1. C. Arnold, *Macromol. Rev.*, **14**, 265 (1969).
2. J. Jachowicz, M. Kryszewski, and A. Sobol, *Polymer*, **20**, 995 (1979).
3. A. S. Hay, in *Encyclopedia of Polymer Science and Technology*, H. Mark, N. G. Gaylord, and N. Bikales, Eds., Wiley, New York, 1969, Vol. 10, p. 92.
4. A. S. Hay, *Adv. Polym. Sci.*, **4**, 496 (1967).
5. R. C. Bopp, U. Gaur, R. P. Kambour, and B. Wunderlich, *J. Therm. Anal.*, **25**(2), 243 (1982).
6. T. P. Jauhiainen, *Angew. Makromol. Chem.*, **104**, 117 (1982).
7. I. Cabasso, J. Jagur-Grodzinski, and D. Vofsi, *J. Appl. Polym. Sci.*, **18**, 1969 (1974).
8. K. Chander, R. C. Anand, and I. K. Varma, *Angew. Makromol. Chem.*, **127**, 137 (1984).
9. V. Percec and B. C. Auman, *Makromol. Chem.*, **185**(11), 2319 (1984).
10. A. J. Chalk and A. S. Hay, *J. Polym. Sci. A1*, **7**, 691 (1969).
11. S. Xie, W. J. Macknight, and F. E. Karasz, *J. Appl. Polym. Sci.*, **29**(8), 2679 (1984).
12. S. S. Mahajan, B. D. Sarwade, and P. P. Wadgaonkar, *Polym. Bull.*, **20**, 153 (1988).
13. S. Percec, *J. Appl. Polym. Sci.*, **33**(1), 191 (1987).

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