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Tri-n-butyltin hydride reduction of the end group of a polyphenylene ether

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Summary

A method using tri-n-butyltin hydride to reduce the 2-methyl-6-(N,N-di-n-butylamino)methyl phenol end group on PPO® (4) was developed. It generated a polyphenylene ether (PPE) with 2,6-xylenol as the only phenolic end group without causing any significant increase in molecular weight.

Introduction

PPE made from Cu/di-n-butyl amine catalyst, oxygen and 2,6-xylenol showed an intrinsic viscosity (I.V.) increase after compression molding. This phenomenon was attributed to the instability of the end groups. The unstable group was identified to be a structure of o-(di-n-butylamino)methyl phenol, a quinone methide precursor at high temperature.((1) and (2)) The incorporation of amine catalyst into the chain end may also be the culprit for the inhibition of the polymer chain growth during the polymerization. Thus, it is desirable to obtain a PPE with 2,6-xylenol as the only phenolic end group to corroborate these findings.

Experimental

Commercially available compounds were used as received without further purification, unless otherwise noted. Melting points were obtained on a Thomas Hoover apparatus and are uncorrected. NMR spectra were obtained with a Varian XL-200(^{1}H NMR, 200 MHz) spectrometer and a Varian EM-390 (^{1}H NMR, 90 MHz) spectrometer relative to an internal tetramethylsilane standard. The procedure for recording ^{31}P NMR spectra was mentioned in a previous paper.(2) High resolution mass spectra were recorded on a MAT 731 spectrometer at a resolution of 10000 (10% valley). Fourier transform infrared spectra were obtained with a Nicolet 7199 spectrophotometer at one wavenumber resolution using CS_2 as the solvent for PPE resin. The concentration of the hydroxyl group at 3610 cm^{-1} was expressed as weight fraction of PPE resin. GPC measurements were performed on a Waters Associates, Inc., LC, Model ALC/GPC 244, equipped with μ-STYRAGEL™ columns in chloroform. A combination of 10^5, 10^4, 10^3, and 500 A columns were used and calibrated with polystyrene standards. A UV detector at 254 nm was employed using chloroform as the eluent.

Tri-n-butyltin hydride reduction of 2-(N,N-di-n-butylamino)-methyl-4,6-dimethylphenol(1)

To a 100 mL flask equipped with a condenser and a stirring bar were added 1.31 g (0.005 mol) of 1, 0.03 g of 2,2'-azobis(3-methylpropionitrile) (AIBN) and 2.16 g (0.0074 mol) of tri-n-butyltin hydride under nitrogen. The reaction mixture was heated to 210°C for half an hour,and GLC(3) indicated that the starting material 1 disappeared completely and mesitol was the only product observed. After cooling the reaction was diluted with water and extracted with ether. The organic layer was separated ,dried($MgSO_4$) and concentrated in vacuo. The pure mesitol was obtained in 85% yield after flash chromatography purification (silica gel, 25% ether in pet ether 35-60°C).The mesitol recovered has the same physical properties as an authentic sample.

Synthesis of 1-methoxy-2-(N,N-di-n-butylamino)methyl-4,6-dimethylbenzene (2)

To a three-necked flask equipped with a condenser, a stirring bar and a nitrogen inlet were added 2.62 g(0.01 mol) of 1 and 30 mL of toluene. Under nitrogen 0.4 g (60% in mineral oil, 0.01 mol) of sodium hydride was added portionwise at room temperature. After hydrogen evolution ceased, the reaction was quenched with 1.64 g (0.01 mol) of methyltrifluoromethanesulfonate. The reaction was slightly exothermic and salt precipitated out immediately. The reaction was stirred at room temperature for another hour before pouring into water. The organic layer was separated ,dried ($MgSO_4$) and concentrated in vacuo. The residue was distilled to give 1.5 g (55% yield) of pure 2: b.p. 105-107°C (0.1 mm);^1H NMR ($CDCl_3$) 0.9 (br m, 6H), 1.0-1.7(br m, 8H), 2.2 (s, 6H), 2.4(t, 4H), 3.7 (s, 2H), 6.8 (s,1H), 7.1(s, 1H); FT-IR (neat) 1240, 1483, 2960 cm^{-1}; HRMS calcd for $C_{18}H_{31}NO$ 277.2406; found, 277.2416.

Tri-n-butyltin hydride reduction of PPE

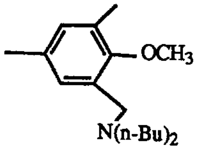
To a 100 mL three-necked flask equipped with a condenser, a nitrogen inlet and a stirring bar were charged 5.0 g of PPE(4), 40.0 g of diphenyl ether, 2.91 g (0.01 mol) of tri-n-butyltin hydride and 0.1 g of the radical initiator AIBN. The mixture was refluxed at 250°C overnight under nitrogen. and the reaction product was precipitated with methanol. After washing three times in methanol, the polymer fluff was collected and dried.

A control experiment was conducted by refluxing 5.0 g of PPE resin in 40.0 g of diphenyl ether under nitrogen at 250°C. The precipitated polymer fluff was collected and dried.

Results and Discussion

PPE synthesized from Cu/di-n-butylamine catalyst is usually composed of two types of phenolic end groups, 3 and 4. The amine-containing end group 4 affects thermal treatment and chemical modification of PPE because of its high reactivity. A post-treatment procedure was therefore sought to replace the amine functionality with a hydrogen and still maintain the integrity of the original PPE. A literature procedure (5) using hydrogen and catalyst to achieve this reduction on simple phenols was reported. The hydrogenolysis procedure required high pressure and high temperature , and the yield was only moderate. Other methods included methanolic sodium methoxide (6) and zinc dust (7) but were conducted in solvents in which PPE is insoluble. Obviously a new process was needed to effectively perform this reduction on a small concentration of polymer end groups.

It was found that tri-n-butyltin hydride reduced 2-(N,N-di-n-butylamino)methyl-4,6-dimethylphenol (1), a model compound for the end group 4 of PPE, at $210^{\circ}C$ in ten minutes to mesitol in 85 % yield after purification.(eq.1) The reduction may go through quinone methide intermediate, as neat tri-n-butyltin hydride cannot reduce N,N-dimethylbenzylamine under the same conditions. Similarly, the reaction between tri-n-butyltin hydride and 2, the methyl ether of 1 , resulted in a complex mixture. Moreover, tri-n-butyltin hydride is well-known for its reduction of α,β-unsaturated ketones (8). Triphenyltin hydride (9), a reducing agent for benzylamines,only generated dark resin material during its reaction with 1.



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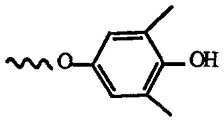

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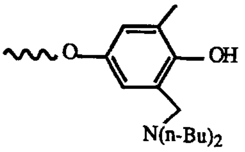

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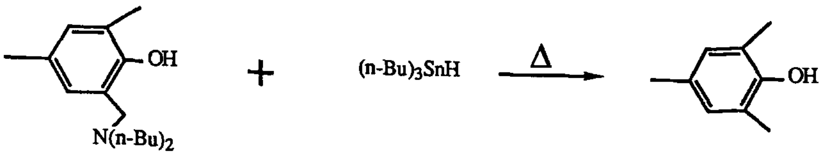

(eq. 1)

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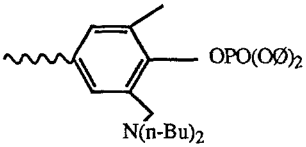
With the facile reduction in hand, the next step was to proceed directly to the reduction of PPE. The reduction was carried out in diphenyl ether under nitrogen overnight at $250^{\circ}C$. The reduced PPE 5 was collected and dried. A control experiment was also conducted under the same conditions without tin hydride to give polymer 6. The properties of original PPE, 5 and 6 are listed in Table I.

Table I. Selected properties of original PPE, 5 and 6

property	**original PPE**	**5**	**6**
OH content at 3610 cm^{-1}	0.089%	0.1516%	0.1117%
Nitrogen	0.12%	0.0377%	0.0458%
I.V.	0.51	0.489	0.622
MW (no.ave.)	19247	20650	26743
MW (wt.ave.)	63585	57689	85098

The IR absorption at 3610 cm^{-1} is an indication of phenolic end group 3, whereas no sharp absorption can be assigned to the hydroxyl stretching of 4 because of hydrogen bonding between nitrogen and the hydroxyl group. After reduction, the one fold increase of 3 as seen by IR through the consumption of 4 was significant. This was further supported by the reduction of nitrogen content in 5 from 1200 ppm to 377 ppm. Above all, the molecular weight of reduced PPE (5) was intact based on intrinsic viscosity (I. V.) and GPC measurements. On the other hand,a simple thermal process in the absence of tin hydride produced a polymer 5 with much higher molecular weight. It also removed, to a lesser extent, the end group 4 as found by comparing the hydroxyl and nitrogen contents of 6 with those of the original PPE.

The polymer 5 was capped with chlorodiphenyl phosphate(2), and a ^{31}P NMR spectrum was taken of the end-capped polymer 7 using CDCl$_3$/CF$_3$COOH (1:1 by vol.) as a solvent. As anticipated, only one peak at -17.75 ppm was observed. The original PPE resin has two major ^{31}P NMR peaks after end-capping with chlorodiphenyl phosphate. They appeared at -13.8 ppm and -17.5 ppm, corresponding to the end group 8 and 9 , respectively.



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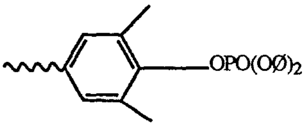

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From the hydroxyl group increase (75%), the nitrogen content decrease (69%) and the end group ^{31}P NMR analysis, it is concluded the di-n-butylamino group at the end of PPE has been replaced by hydrogen. This replacement is significant, if not complete, by this reduction technique. The scope and the mechanism of this reduction will be published in the near future.

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3. The reaction mixture was silylated with bis(trimethylsilyl)-trifluoroacetamide before injecting into the GLC because of the thermal instability of compound 1.
4. PPO®, a polyphenylene ether, is a registered trademark of the General Electric Company. It is a homopolymer of 2,6-xylenol, having a number average molecular weight of 15,000-20,000.
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