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A ^{31}P NMR study of poly(phenylene oxide) (PPO)(1) resin's hydroxyl end groups

Herbert S.-I. Chao

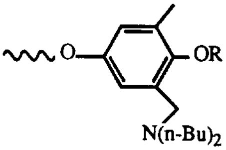
General Electric Corporation Research and Development Center, Schenectady, NY 12301, USA

SUMMARY

The hydroxyl end groups of PPO resin, made from Cu/di-n-butylamine, 2,6-xylenol and oxygen ,were capped with diphenyl chlorophosphate. A ^{31}P n.m.r. method was developed to distinguish the 2,6-xylenol and 2-methyl-6-(N,N-di-n-butylamino)methyl phenol end groups, which are directly related to the resin's thermal stability.

INTRODUCTION

The preparation of poly(2,6-dimethyl-1,4-phenylene oxide) can be achieved through various monomers and reaction conditions (2). Several patented processes using copper/di-n-butyl amine as a catalyst (3) with 2,6-xylenol and oxygen produce PPO resin with especially desirable properties. These resins contain the head end groups of structure 1 with the secondary amine incorporated as well as the regular head end groups 2 (4). End groups of structure 1 may be responsible for some of the interesting properties of the resin because of the possibility of decomposing to form a reactive quinone methide at the processing temperature. We would like to report a ^{31}P n.m.r. method to distinguish and quantify 1 and 2 by capping the hydroxyl groups with diphenyl chlorophosphate.



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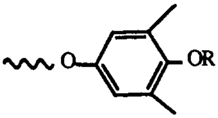
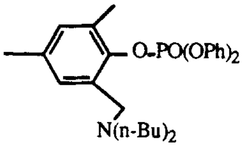
3 R = $PO(OPh)_2$



2 R = H

4 R = $PO(OPh)_2$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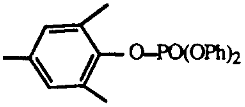
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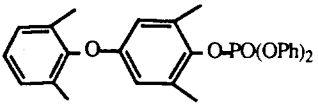
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EXPERIMENTAL

All 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-300 (^{1}H NMR, 300 MHz) spectrometer and a Varian EM-390 (^{1}H NMR, 90 MHz) spectrometer relative to an internal tetramethylsilane standard. Phosprorous NMR spectroscopy was done on a 121.4 MHz (7.1-T) Varian XL-300 instrument in 10-mm NMR tubes. Chemical shifts for phosphrous-containing compounds were reported as positive upfield relative to external 85% phosphoric acid. Integration was done overnight with chromium acetylacetonate added as a relaxation agent.

Synthesis of 5. To a one-necked round bottom flask equipped with a stirring bar were charged 13.12 g (0.05 mol) of 2-(N,N-di-n-butylamino)methyl-4,6-dimethylphenol, 13.43 g(0.05 mol) of diphenyl chlorophosphate and 100 mL of THF. To this homogeneous solution was added 10.1g (0.1 mol) of triethylamine dropwise at room termperature. After the addition was complete, the stirring continued for another five hours. The ammonium chloride salt was removed by filtration, and the filtrate was concentrated in vacuo to yield an oil which still contained some salt. It was diluted with pentane, and to this pentane solution was added a small amount of silica gel. The mixture was filtered through Celite ,and the crude compound 5 was obtained as an oil by evaporating the solvent in vacuo. ^{1}H NMR($CDCl_3$): 0.7-1.0 (br m, 6H), 1.0-1.4 (br m, 8H), 2.2-2.4 (br d, 6H), 3.5 (s,2H), 6.8 (br s,2H), 7.0-7.4 (br m,10H).

Synthesis of 6. Compound 6 was made from mesitol , diphenyl chlorophosphate and triethylamine in a similar fashion as the compound 5 : m.p. 65-66 °C (recrystallized from n-heptane); ^{1}H NMR ($CDCl_3$): 2.20(s, 3H), 2.30 (s, 6H), 6.81(s, 2H),7.21(br s, 10 H).

Typical capping procedure. Five grams of PPO resin were dissolved in 100 mL of toluene, and to this solution 1 g of diphenyl chlorophosphate and 1 g of triethylamine were added. The reaction was stirred at room temperature overnight, and the polymer was precipitated from methanol or anhydrous acetonitrile. After drying at room temperature overnight the polymer was again dissolved in CH_2Cl_2 to form a complex which precipitated out gradually at 0 °C. The complex was filtered and dried in preparation for NMR measurement.

RESULTS AND DISCUSSION

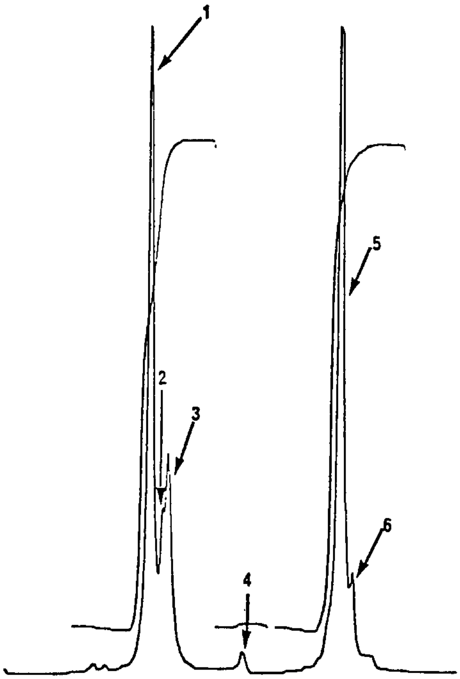
The end group capping technique with diphenyl chlorophosphate has been used (5) to determine the structure of active centers in anionic polymerization of several polymers by ^{31}P n.m.r. Similarly in PPO resin, after capping 1 and 2 with diphenyl chlorophosphate we may be able to distinguish the resulting structures 3 and 4 through ^{31}P n.m.r. The model compounds 5 and 6 were prepared, but unfortunately their ^{31}P n.m.r. chemical shifts in d-chloroform were indistinguishable (Table I). As expected, the ^{31}P n.m.r. of diphenyl phosphoryl-capped PPO resin 8 in d-chloroform did not offer any extra information except a sharp peak at

Table I. ^{31}P n.m.r. Chemical Shift

Compound	Solvent*	^{31}P Chemical Shift (ppm)
5	A	-16.94
6	A	-16.94
8	A	-16.67
5	B	-14.19
6	B	-17.28
7	B	-17.22

* A: $CDCl_3$; B: $CF_3COOH/CDCl_3$ (1:1 by volume)

-16.67 ppm representing 3 and 4. Since the chemical shift of ^{31}P n.m.r is very sensitive to structure variations, we expected that an acidic solvent which protonated the amine should produce some change in chemical shift of 3, while not affecting 4. In a trifluoroacetic acid / d-chloroform mixture (1:1 by volume) the ^{31}P n.m.r. signal of 5 shifted to lower field at -14.19 ppm, while the shift of 6 remained nearly unchanged (Table I). Another model compound 7 (6) has a ^{31}P n.m.r. chemical shift at -17.22 ppm, which indicated that substitution at the para position of the aromatic ring does not have a large influence on the ^{31}P n.m.r. chemical



Index	ppm
1	-13.84
2	-14.08
3	-14.16
4	-15.62
5	-17.43
6	-17.67

Fig 1. ^{31}P n.m.r. spectrum of 8 in $CF_3COOH/CDCl_3$ (1:1 by volume)

shift of the phosphate attached. With all the model compound information in hand, the ^{31}P n.m.r. of diphenyl phosphoryl-capped PPO resin 8 was measured in the same solvent mixture. The spectrum with the assignment is reproduced in Figure 1. This sample had comparable amount of head end groups 4 and 3 if we assumed that the capping reaction was quantitative. The structures attributed to the four minor absorptions at -14.08, -14.16, -15..62 and -17.67 ppm are still under investigation.

When the same PPO resin was extruded at 300 °C, an I.V. (intrinsic viscosity) increase was observed (4) which has been attributed to a reaction resulting from the decomposition of 1. The extruded sample was treated with diphenyl chlorophosphate, and a ^{31}P n.m.r. spectrum was taken on the resulting capped polymer 9. Indeed, only one major peak at -17.40 ppm was detected indicating the total absence of the amine-containing end group.

This ^{31}P n.m.r. method has enabled us to distinguish the minute quantities of different PPO resin end groups, and it certainly will help the understanding of the novel chemistry of PPO resin.

ACKNOWLEDGMENT

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