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Facile Quantitative Analysis of Hydroxyl End Groups of Poly(2,6-dimethyl-1,4-phenylene oxide)s by ^{31}P NMR Spectroscopy

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ABSTRACT: Phenolic compounds can be readily phosphitylated with 1,3,2-dioxaphospholanyl chloride (9; Scheme 1) directly in an NMR tube. Using ^{31}P NMR spectroscopy different phenols can be easily discriminated. Using this technique we have developed a facile qualitative and quantitative method for the determination of phenolic functional groups in PPO resin. On the basis of the developed technique, we were able to obtain the hydroxyl concentration of normal phenolic ends, hydrogen-bonded phenolic ends, and phenolic groups on the backbone, as well as the number-average molecular weight of the polymers. In addition, based on nitrogen content analyses and quantitative ^{31}P NMR, the Mannich type ends were also determined. The precision of the method was determined to be ± 15 ppm for the determination of individual hydroxyl functionalities. The results of quantitative ^{31}P NMR when compared to those obtained by applying traditional analytical techniques were in excellent agreement.

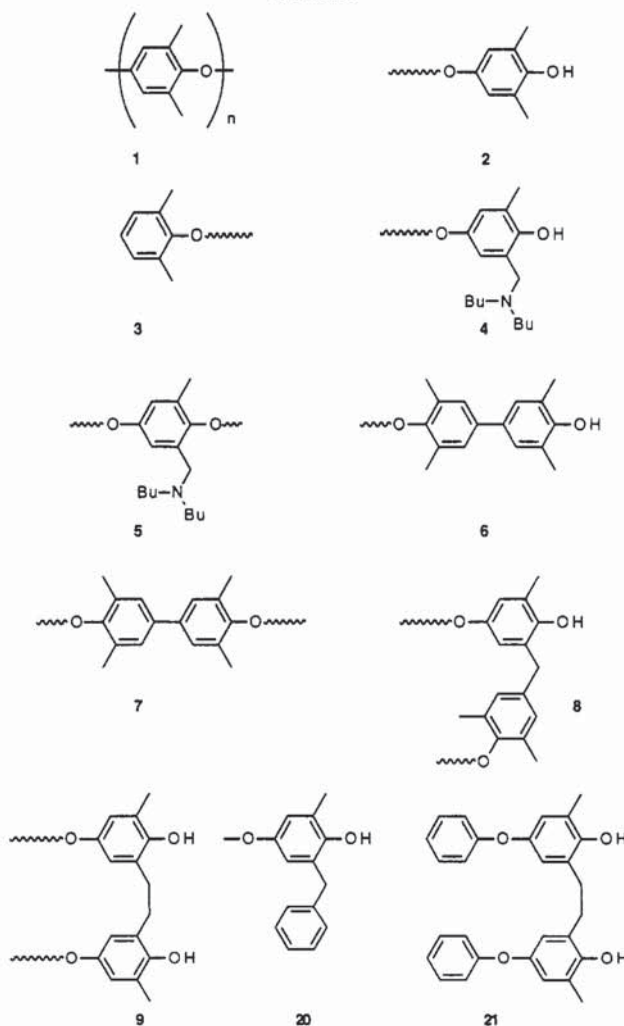
Introduction

Poly(2,6-dimethyl-1,4-phenylene oxide), PPO resin, is an important engineering thermoplastic due to its high T_g , tensile strength, stiffness, impact strength, and creep resistance.¹ Noryl resin, which is a blend of PPO and polystyrene, is one of five major engineering thermoplastics manufactured today. PPO is usually prepared by oxidative coupling polymerization of 2,6-dimethylphenol in the presence of an amine-complexed copper (I) catalyst and oxygen at ambient temperature.²

^{13}C NMR has been proven to be very useful in identifying repeat unit 1, end groups 2 and 3, and units 5–9 in the polymer^{3–8} (Chart 1). However, due to the insensitivity of the ^{13}C nucleus for NMR studies and the low concentration of most of these units, it is still impractical to use it as a routine and reliable analytical tool to determine the concentration of these units.

Since most of the trace structural units in PPO resin contain labile phenolic hydroxyl groups, it was thought that these functional groups could serve as a handle for attaching a more sensitive NMR nucleus which would give stronger and well-separated signals for the different structural units. The particular nucleus that we have studied is phosphorus, because it is 377 times more sensitive than carbon.⁹ Phosphorus has a large range of chemical shift, ~ 700 ppm, which ensures a good separation of signals of the ^{31}P nuclei in different environments. Furthermore, it is well-known that derivatization of a phenolic group with phosphorus halides is quantitative and rapid. This is very significant in order to ensure reliable quantitative results. Finally there are no interfering phosphorus atoms within the PPO resin which simplifies the assignment of the spectra. Diphenyl chlorophosphate has been used previously to derivatize PPO hydroxyl groups, with some success in differentiating the various hydroxyls groups using ^{31}P NMR. However, the

Chart 1



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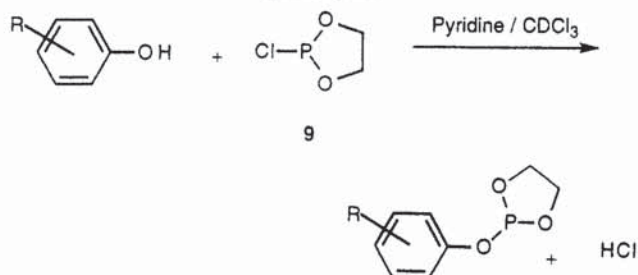
[§] GE Corporate Research and Development.

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esterification reaction required was relatively cumbersome and needed to be performed on a large scale.¹⁰

Earlier work¹¹ has demonstrated that a large variety of phenolic^{11a} and carbohydrate^{11b} model compounds and

Scheme 1. Reaction Used to Quantitatively Derivatize the Labile Protons Present in PPO Model Compounds and Resins



lignins^{11c} derivatized with 1,3,2-dioxaphospholanyl chloride (9; Scheme 1) can be qualitatively and quantitatively^{11d} analyzed by ³¹P NMR spectroscopy. Furthermore, the derivatization can be easily carried out directly within an NMR tube. In this paper we now report the development of a facile qualitative and quantitative method for the determination of phenolic functional groups in PPO resins by first derivatizing them with the chloride 9 to give a phosphite ester followed by analysis of the derivatized material by ³¹P NMR spectroscopy.

Results and Discussion

Model Compound Study. In order to assign the signals that will appear in the spectra of derivatized PPO resins, a number of model compounds have been selected and derivatized with the chloride 9 and their ³¹P chemical shifts were determined (Table 1).

Compounds 10a–d are models for the normal phenolic end 2 of PPO. Compounds 11a and 11b are models for the phenolic end 4. Compounds 12 and 13 are models for the biphenyl end 6. Compound 14 is a model for the backbone phenolic group 8. Compounds 15–19 are used to model unhindered phenolic ends that might appear in the PPO resin.

The ³¹P chemical shifts of different types of phenolic end models were well separated from one another (Figure 1), with the exception that the unhindered phenolic end model compounds 17–19 all appeared at 128.2 ppm and were not well resolved. The derivatives of all 2,6-disubstituted phenolic model compounds gave well-separated signals in the region of 130–132 ppm (Figure 1). Models of the same type gave the same chemical shift.

An interesting observation is that within the same type of model compounds those with a phenoxy group at the para-position with respect to the phenolic group have a higher chemical shift (~0.5 ppm) than those without (e.g., compare 10b–d to 10a, or 11b to 11a). This is probably due to the electron-donating nature of the phenoxy group which increases the induced ring current of the phenyl ring and hence results in a stronger deshielding effect upon the phosphorus nucleus. It was also found that the chemical shifts of models with normal phenolic end groups were independent of the chain length, and all have chemical shifts at 131.2 ppm.

PPO Resin Samples. Two types of PPO resins have been investigated. The first sample was an original PPO resin (as isolated) for which two signals were identified at 131.0 and 131.2 ppm. The second sample was an extruded PPO resin (extrusion temperature was 300 °C), for which two signals were identified at 131.2 and 132.1 ppm. By comparing the chemical shift values of these signals with those of the model compounds, it became apparent that both samples had one common signal at 131.2 ppm which indicated the presence of a normal phenolic end 2 in the polymer. Finally, the signal at 132.1 ppm of the extruded

Table 1. ³¹P Chemical Shifts of Phenols Derivatized with Chloride 9

phenol		chemical shift (ppm)
	10a	130.66
	10b	131.23
	10c	131.24
	10d	131.21
	11a	130.23
	11b	131.00
	12	130.72
	13	130.72 / 131.26
	14	131.47
	15	131.50
	16	131.18
	17	128.30
	18	128.24
	19	128.24

PPO resin may indicate the presence of backbone phenolic groups 8 and 9 (Figure 2). Even though we do not have perfect models, i.e., 20 and 21 for this kind of structure, we do have models 14 and 15 which gave ³¹P chemical shifts of 131.5 ppm upon derivitization (Table 1). As already mentioned, the addition of a phenoxy group on the para-position of a model compound increases the ³¹P chemical shift by 0.5 ppm. Models 20 and 21 which are different from 14 and 15 by a *p*-phenoxy group should therefore have chemical shifts at ~132 ppm.

Therefore, there were only three major signals found in PPO samples. Other minor signals have also been observed (especially when the acquisition time was prolonged) which

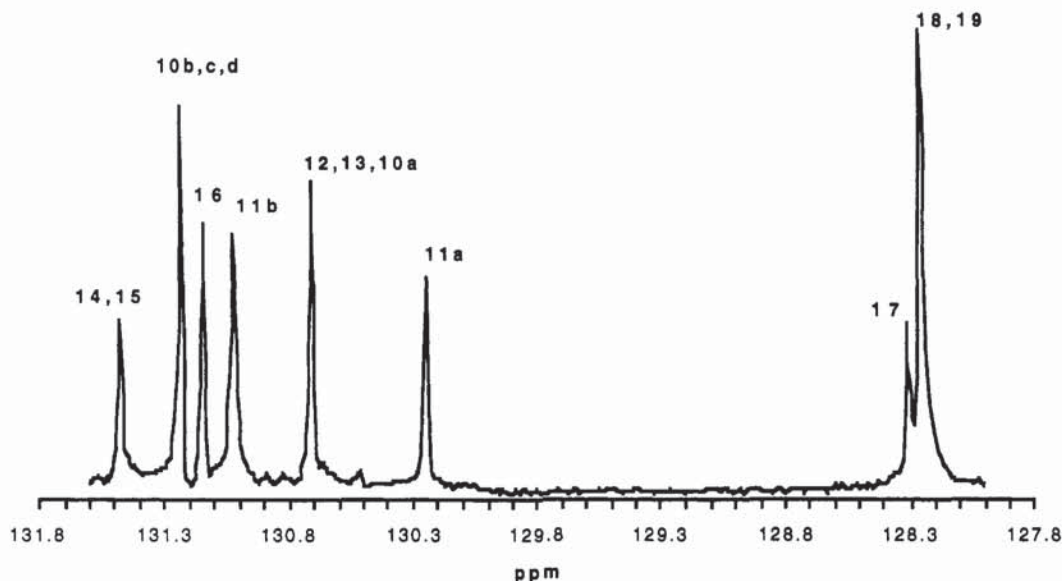


Figure 1. ^{31}P NMR spectra of a mixture of derivatized phenolic model compounds resembling PPO end groups. The numbers correspond to the compounds identified as such in Table 1.

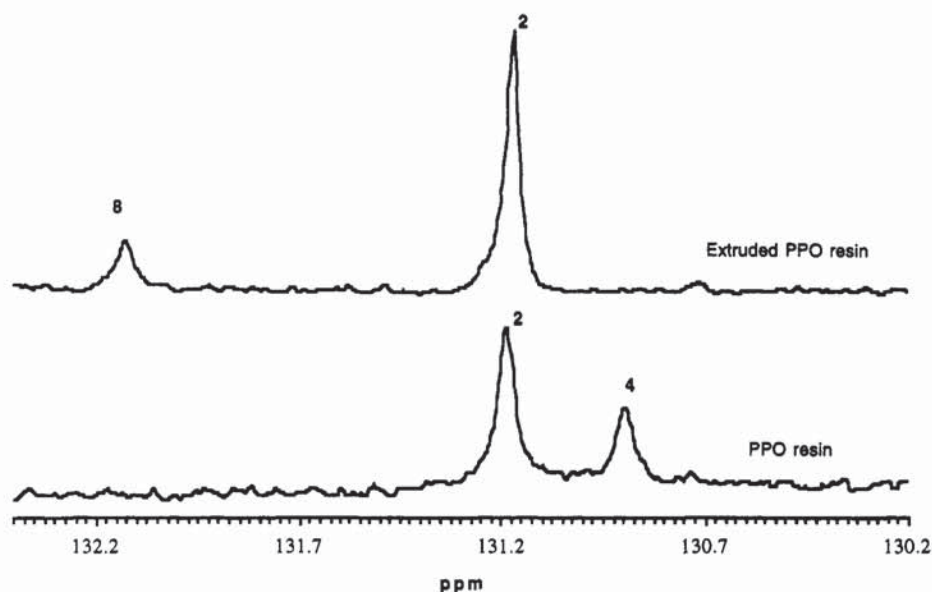


Figure 2. ^{13}P NMR spectra of PPO polymers derivatized with chloride 9. Acquisition conditions: continuous proton decoupling, 45° flip angle, acquisition time 0.5 s, no pulps delay time. Total acquisition time 1 h, on a Varian XL300 spectrometer.

may indicate the presence of other phenolic ends in the polymer but present in much lower concentrations. Current efforts are focused at increasing the detection limits so that other possible phenolic end groups can be identified and quantified.

Quantitative Analysis of PPO and Its Blend. The use of FT NMR methods of analysis is showing considerable promise with regard to their reliability as analytical tools. The integration of the NMR signal is proportional to the concentration of the nucleus if appropriate experimental conditions are observed.^{11d,16}

In order to measure the amount of each phenolic end present in the PPO resin by ^{31}P NMR, a suitable compound for use as an internal standard was required. By introducing a known amount of standard to a known amount of PPO resin, the concentration of phenolic ends can be calculated based on the integration ratio of the sample and internal standard signal. Bisphenol A (BPA) was found to be a suitable internal standard in our study.^{11d}

Derivatized BPA gave a ^{31}P signal at 128.3 ppm, with a spin-lattice relaxation time (T_1) of 7 s (at 121.5 MHz).

This is a region that does not overlap with any major signals in the region of interest. Phosphorus nuclei attached to the polymer were found to have a spin-lattice relaxation time of less than 1 s. Therefore, in order to obtain valid analytical results (within a 10% error margin), 1.3 times the largest T_1 between successive 45° pulses must be employed.¹⁷ This dictated the use of a delay time of 10 s.¹⁸ Intensity distortion due to proton to phosphorus nuclear Overhauser effects and proton-phosphorus scalar couplings were eliminated by employing an inverse-gated proton decoupling sequence during acquisition.^{11d,19}

A series of quantitative analyses were carried out on three different samples which can be identified as follows: (A) PPO resin, (B) PPO and polystyrene alloy blend (1:1, w/w; PPO/PS), (C) PPO and high impact polystyrene alloy blend (1:1, w/w; PPO/HIPS). Results are summarized in Table 2.

On the basis of our technique, we are able to obtain the hydroxyl concentration of normal phenolic ends 2, phenolic ends 4, and phenolic groups on the backbone 8 or 9, as well as the number-average molecular weight of the polymers.

Table 2. Results of ^{31}P Quantitative Analyses Obtained for Three PPO Resins Using Chloride 9 as the Derivatizing Reagent

	(A) PPO resin ^a	(B) PPO/PS ^a	(C) PPO/HIPS ^a
(1) % of OH on normal phenolic end	0.087	0.045	0.042
(2) % of OH of phenolic end 4	0.039	not detected	not detected
(3) % of OH on backbone phenolic group	not detected	0.011	0.010
(4) % of total OH groups	0.126	0.056	0.052
(5) % N on phenolic end	0.034	not detected	not detected
(6) M_n ^b	13 400	18 700	20 200

^a Percentage values are expressed as w/w. ^b M_n of the PPO in the blend is based on the % wt of PPO.

Table 3. Results of Traditional Quantitative Analyses Carried out on Three PPO Resins

	(A) PPO resin	(B) PPO/PS	(C) PPO/HIPS
(1) % of OH ^a	0.090	0.055	0.051
(2) % of N ^b	0.106	0.062	0.051
(3) M_n ^c	12 500	21 200	23 600
(4) M_w ^c	48 070	74 150	72 800

^a % OH was determined by FT-IR.¹² ^b % N was determined by an automated Dumas method using a Carlo-Erba NA1500 nitrogen analyzer. ^c Molecular weight was determined using a Waters GPC equipped with four μ -Styragel columns (10^5 , 10^4 , 10^3 , 500 Å) attached to a UV detector using monodisperse polystyrenes as calibration standards.

In addition, the nitrogen content present in the phenolic end 4 can also be calculated. The analysis was repeated three times for each sample; therefore, the precision of the method was thus determined to be $\pm 0.0015\%$ or ± 15 ppm for the determination of the hydroxyl functionality. These results were then compared with those obtained by applying traditional analytical techniques (Table 3).

Apparently the OH content determined by quantitative ^{31}P NMR was in good agreement to that obtained by the IR method. One limitation of the IR method is that non-hydrogen-bonded phenolic hydroxyl groups can be detected. Phenolic ends 4 cannot be detected, because of intramolecular hydrogen bonding between the nitrogen and the phenolic group. However, the described technique can detect all types of phenolic hydroxyls. For example, sample A (Table 2) showed a total OH content of 0.126% using quantitative ^{31}P NMR, while it showed 0.090% by the IR method. The latter value is very close to that obtained for normal phenolic end groups (0.087%) determined by quantitative ^{31}P NMR (Table 2).

Determinations using the Dumas method²⁰ gave the total nitrogen contents of the polymers, while the ^{31}P NMR method determined selectively those nitrogens that appeared in phenolic ends 4 of the polymer. The combination of these two techniques permits a more detailed analysis of nitrogen distribution within the polymer.

Finally the excellent correlation of number-average molecular weights (M_n) determined by quantitative ^{31}P NMR (Table 2) and gel permeation chromatography (Table 3) is notable.

Experimental Section

Compound 10a was obtained from the Aldrich Chemical Co. Compounds 10c and 10d were synthesized according to ref 12, and compounds 10b, 17, and 18 were synthesized according to ref 13. Compound 11a was synthesized according to ref 5. Compounds 12 and 13 were synthesized according to ref 6. Compound 14 was synthesized according to ref 8. Compound 15 was synthesized according to ref 14. Compound 16 was synthesized according to ref 15. PPO samples, a PPO-polystyrene alloy blend (1:1, w/w; PPO/PS), and a PPO-high impact polystyrene alloy blend (1:1, w/w; PPO/HIPS) were obtained from General Electric Co. The derivatizing reagent, 1,3,2-dioxaphospholanyl chloride (9), was obtained from Fluka Chemical Co. The pyridine used was analytical grade.

2-[(Di-*n*-butylamino)methyl]-4-(2,6-dimethylphenoxy)-2-methylphenol (11b). 4-(2,6-Dimethylphenoxy)-2-methylanisole was prepared by the Ullman ether condensation reaction by adding a 40% solution of 4-bromo-2-methylanisole in DMF to an equimolar quantity of potassium 2,6-dimethylphenoxide (from 2,6-dimethylphenol and potassium *tert*-butoxide in an equal weight of DMF by distilling off *tert*-butanol) with CuBr catalyst (20 g of CuBr/mol of bromoanisole) under anhydrous conditions and a nitrogen atmosphere. After 3 h at reflux the reaction mixture of methanol, ice, and concentrated hydrochloric acid was then extracted with ether. After removal of the ether the product was dissolved in hexane and extracted with Claisen's alkali to remove unreacted starting phenol. Vacuum distillation afforded a 50% yield of pure 4-(2,6-dimethylphenoxy)-2-methylanisole. ^1H NMR: δ 0.88 (t, $J = 7.2$ Hz, 6 H), 1.30 (sext, $J = \sim 7.4$ Hz, 4 H), 2.12 (s, 6 H), 2.16 (s, 3 H), 2.46 (t, $J = 7.5$ Hz), 3.61 (s, 2 H), 6.20 (d, $J = 3$ Hz, 1 H), 7.06 (m, 3 H), 11.1 (br s, 1 H). ^{13}C NMR: δ 13.92, 15.99, 16.46, 20.53, 28.24, 53.09, 57.94, 111.80, 115.74, 122.15, 124.58, 126.09, 128.86, 131.63, 150.13, 150.24, 151.72.

4-(2,6-Dimethylphenoxy)-2-methylphenol (18) was prepared by heating 4-(2,6-dimethylphenoxy)-2-methylanisole (5.0 g, 20.7 mmol) in 15 g of anhydrous pyridine hydrochloride for 1 h at the refluxing temperature. The molten mixture was added to ice water, recrystallized from a mixture of benzene and hexane, and then dried to give 18 (yield 3.77 g, 80%, mp 153–154 °C). ^1H NMR: δ 2.15 (s, 6 H), 2.18 (s, 3 H), 3.78 (s, 3 H), 6.37–6.73 (m, 3 H), 7.07 (s, 2 H). ^{13}C NMR: δ 16.4 (3 benzylic methyls), 55.7, 110.8, 111.5, 117.3, 124.7, 128.0, 128.9, 131.6, 151.6, 152.3 (2 ether C's).

4-(2,6-Dimethylphenoxy)-2-methylphenol (18) (0.10 g, 0.44 mmol), di-*n*-butylamine (0.62 g, 0.48 mmol), and aqueous formaldehyde (37%, 0.41 g, 0.50 mmol) were stirred at 25 °C for 1 h and then heated at 80 °C for 1 h with an oil bath. Volatile products were removed at reduced pressure with a rotary evaporator from the crude product. Liquid chromatography (LC with GPC columns) displayed one major peak and a small starting material peak. Purification by HPLC provided material with one peak by LC and spectral analyses consistent with structure 11b. ^1H NMR: δ 2.12 (s, 6 H), 2.18 (s, 3 H), 6.40 (dd, 1 H), 6.56 (d, 1 H), 6.67 (d, 1 H), 7.09 (m, 3 H). ^{13}C NMR: δ 16.0, 16.4, 112.4, 115.6, 117.0, 124.8, 125.1, 129.0, 131.6, 148.1, 151.5, 151.8.

2-[(Di-*n*-butylamino)methyl]-4-methoxyphenol (19). A mixture of di-*n*-butylamine (64.5 g, 0.5 mol) and 4-methoxyphenol (62.1 g, 0.5 mol) was warmed to 35 °C to form a clear solution, aqueous formaldehyde (37%, 37.6 mL, 40.6 g, 0.5 mol) was added, and the mixture was stirred. During the addition an ice/water bath was used to maintain a temperature of 45–50 °C. After standing for 2 h without the cooling bath, the mixture was heated to 90 °C for 90 min and then cooled and the volatile products were removed with a rotary evaporator. The product was dried over 3 Å molecular sieves and then decanted (yield 126 g). ^1H NMR: δ 0.91 (t, $J = 7.2$ Hz, 6 H), 1.30 (m, 4 H), 1.50 (m, 4 H), 2.48 (dd, $J = 7.4$ Hz, 4 H), 3.70 (s, 2 H), 3.74 (s, 3 H), 6.54 (m, 1 H), 6.76 (s, 1 H). ^{13}C NMR: δ 13.82, 20.44, 28.32, 53.08, 55.5, 58.16, 113.07, 114.25, 116.11, 122.88, 151.21, 151.79 ppm.

Derivatization Procedure. The model compounds or polymer samples (20 mg) were derivatized in a 5-mm NMR tube with 1:1 mixture of CDCl_3 and pyridine as solvent, followed by 20 μL of chloride 9. For quantitative analysis of polymer samples, a typical sample preparation and derivatization was carried out as follows:¹⁴ 600 mg of PPO sample was first dissolved in 5 mL of CDCl_3 in a 10-mL volumetric flask, followed by 1 mL of a pyridine solution of Bisphenol A (4.06 mg/mL), and the solution was made up to 10 μL using pyridine. A total of 400 μL of the above solution

was transferred to a 5-mm NMR tube followed by the addition of 30 μ L of chloride 9. The resulting solution was shaken for 30 min at room temperature prior to analysis.

NMR Spectroscopy. ^{31}P NMR spectra were measured on Varian XL200 and XL300 spectrometers by using a 5-mm broadband probe at 20 °C. The internal lock was provided by CDCl_3 . All signals were referenced to the product of chloride 9 with water,^{11a-d} whose chemical shift was set at 121.1 ppm. For quantitative work, the spectra were acquired on a XL300 machine for 5 h using inverse-gated proton decoupling, a spectral window from 125 to 140 ppm, a pulse angle of 45°, an acquisition time of 1 s, and a pulse delay of 10 s. Peak integration was used for the calculation.

Conclusions

A facile technique has been developed to end-cap the phenolic hydroxyl groups present in PPO resins or its blends with a phosphite group. The quantitative derivatization was carried out rapidly ($1/2$ h) in an NMR tube. ^{31}P NMR spectra of derivatized PPO samples gave well-separated signals, allowing the detection and quantification of normal phenolic ends, amino phenolic ends, and backbone phenolic hydroxyl groups in the polymer. The assignment of these signals was based on a model compound study.

Quantitative analysis of these phenolic groups on three different types of PPO and its blends was realized with high precision by the application of appropriate NMR acquisition parameters, in a manner similar to that applied for the analysis of lignins.^{11d} Hydroxyl contents as low as 100 ppm can thus be detected by the proposed technique. Work is in progress toward improving the sensitivity of the technique, identifying minor signals observed, and extending it to other synthetic and natural polymers.

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