

# Molecular Weight of Poly(2,6-dimethyl-1,4-phenylene oxide) As Determined by $^{13}\text{C}$ NMR Spectroscopy

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**ABSTRACT:** The assignments of the carbon-13 resonances of the chain ends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) have been revised by using chemical shifts induced by the lanthanide shift reagent  $\text{Pr}(\text{fod})_3$ . Molecular weights of PPO samples were obtained from quantitative analyses of the  $^{13}\text{C}$  NMR spectra. A linear correlation between the glass transition temperature and reciprocal molecular weight is observed.

## Introduction

An important factor in many applications of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is the molecular weight or the chain length of the polymer. NMR spectroscopy, in particular  $^{13}\text{C}$  NMR, is an excellent method for the determination of the chain length of linear oligomers (polymers with chains shorter than 50 units). The prerequisites for the application of this approach are observable and properly assigned signals of the chain ends. The assignments of the carbon-13 resonances of the main repeating units<sup>1</sup> and the chain ends<sup>2</sup> of PPO have been published in the literature. However, in attempting to use the assignments of the chain ends for determining molecular weights, we found internal inconsistencies. In particular, a resonance at 151.3 ppm assigned to C-1'' (C-1 of the tail unit) integrates as two carbons rather than one. This report summarizes our approach to the assignment of the chain-end resonances of PPO along with molecular weight data on several samples.

## Results and Discussion

The  $^{13}\text{C}$  NMR spectrum of PPO with assignments is displayed in Figure 1. The five major peaks are due to the units of the main chain; a number of smaller peaks are due to the chain ends. Originally,<sup>2</sup> the peak at 151.3 ppm was assigned to C-1'', while the peak at 154.4 ppm was attributed to C-4 of the head unit. (Note that there is a systematic discrepancy of 0.1–0.3 ppm between the literature values and ours, probably due to different methods of referencing.) It can be seen that the peak at 151.3 ppm is taller than that of C-1 at 146.3 ppm; we found that its integral is twice as large. Also, consideration of substituent effects on carbon-13 chemical shifts in aromatic systems<sup>3</sup> leads to the conclusion that C-4 should be shifted a few ppm upfield relative to C-4', its counterpart in the main chain.

The resonances of the head unit, which has a hydroxyl group, can be discriminated from those of the tail unit and properly assigned with the aid of a lanthanide shift reagent<sup>4,5</sup> such as  $\text{Pr}(\text{fod})_3$ . The shift reagent, which is a Lewis acid, forms a complex at the hydroxyl group, which acts as a Lewis base. In the complex, the paramagnetic lanthanide ion (praseodymium in our case) causes dipolar shifts in the nuclear resonances of the ligand. These shifts are, *inter alia*, inversely proportional to the cube of the distance between the paramagnetic ion and the observed nucleus. Under conditions of rapid (relative to the shift) chemical exchange between the complexed and free ligand, the net lanthanide-induced shift (LIS) increases with increasing the shift reagent concentration at constant

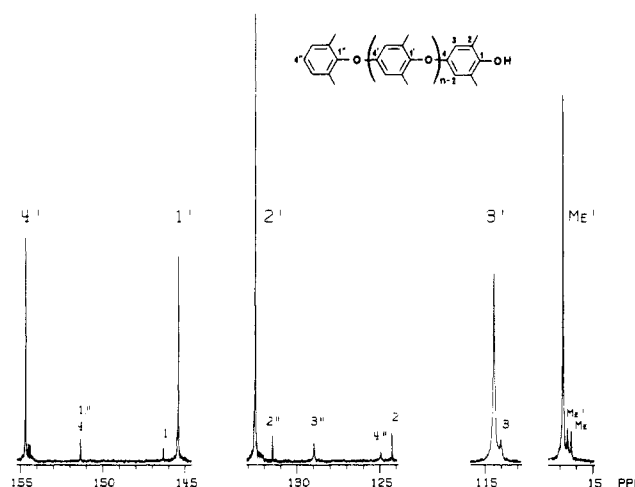


Figure 1.  $^{13}\text{C}$  NMR spectral bands of PPO (sample 2).

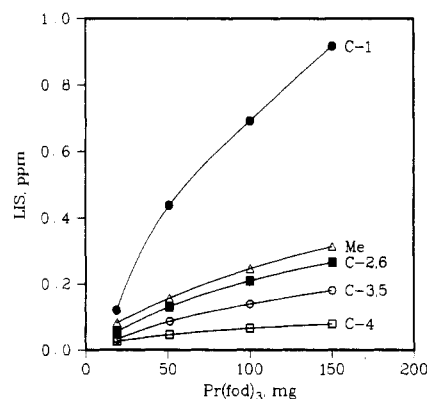


Figure 2. Lanthanide-induced shifts in the carbon-13 resonances of the head unit of PPO as a function of added shift reagent.

ligand concentration. Plots of the LIS against the amount of added  $\text{Pr}(\text{fod})_3$  are shown in Figure 2. Only the resonances of the head unit shifted. As expected<sup>5</sup> for  $\text{Pr}(\text{fod})_3$ , the shifts were to lower frequencies. Most importantly, the small peaks at 154.5 and 154.4 ppm did not shift. They are probably due to C-4' of penultimate units. On the other hand, the resonance at 151.3 ppm splits into two components of equal intensity, only one of which shifted. (As could be anticipated, replacing the deuteriochloroform solvent with perdeuteriobenzene also led to splitting of this resonance.) This phenomenon is illustrated in Figure 3. The shifting component is assigned to C-4.

The methyls of the chain ends of PPO resonating at 16.5 and 16.3 ppm have not been previously assigned. We

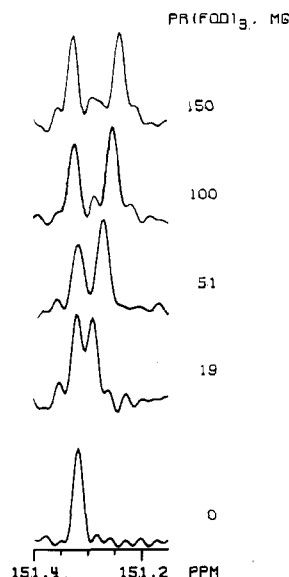


Figure 3. Transformation of the peak at 151.3 ppm with the addition of shift reagent.

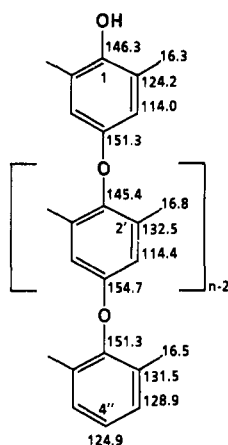


Figure 4. Summary of the carbon-13 chemical shifts of PPO.

found that the latter peak shifted upon the addition of shift reagent and assigned it to the methyls of the head unit. Thus, the peak at 16.5 ppm must be due to the methyls of the tail unit. A summary of the chemical shifts of PPO is shown on the structural formula in Figure 4.

For the molecular weight and chain length determination we chose the spectral region 144–156 ppm, which contains nonprotonated carbons bonded to oxygen. In this way complications due to unequal nuclear Overhauser enhancements are effectively eliminated. The total integrated area of this region corresponds to twice the chain length,  $n$ , less 1 (C-4'' is protonated). Thus

$$I_{(154-144)} = A(2n - 1) \quad (1)$$

The integral of the signal at 151.3 ppm, as mentioned, corresponds to two carbon atoms; viz.

$$I_{(151)} = 2A \quad (2)$$

where  $A$  is a proportionality constant. Solving eqs 1 and 2 for  $n$ , one obtains

$$n = I_{(154-144)} / I_{(151)} + 1/2 \quad (3)$$

The molecular weight of the main unit of PPO is 120 and that of the chain ends is 121. Thus, for the number-average

Table I  
Chain Length, Number-Average Molecular Weight, and Glass Transition Temperature for PPO

quantity	sample			
	1	2	3	4
$n$	$27 \pm 1$	$23 \pm 1$	$18.5 \pm 0.7$	$13.3 \pm 0.5$
$M_n$	$3238 \pm 120$	$2763 \pm 120$	$2226 \pm 85$	$1597 \pm 60$
$T_g, ^\circ\text{C}$	174.9	168.7	149.6	130.9

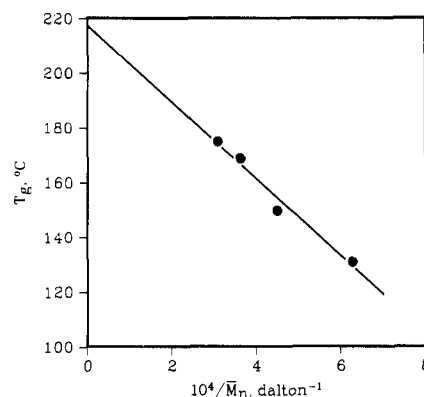


Figure 5. Plot of the glass transition temperature of PPO against the inverse of the number-average molecular weight (determined by  $^{13}\text{C}$  NMR spectroscopy).

molecular weight of PPO, one obtains

$$M_n = 120n + 2 \quad (4)$$

The results obtained for four samples are summarized along with other pertinent data in Table I.

We note that the glass transition temperature,  $T_g$ , shows a linear correlation with the reciprocal of the number-average molecular weight. This is depicted in Figure 5. The line obtained by linear regression analysis is described by

$$T_g (^\circ\text{C}) = 217.3 - 140500/M_n \quad (5)$$

Relationships of this kind were first proposed by Fox and Flory.<sup>6</sup> The linearity indicates that the end groups and the free volume associated with them play the dominant role in governing the glass transition temperature. The free term is the limiting value of  $T_g$  at very high molecular weights. The value of 217.3  $^\circ\text{C}$  obtained from the data analysis is well within the range of 210–234  $^\circ\text{C}$  observed for PPO (the actual value depends on the thermal treatment of the sample).<sup>7</sup>

## Experimental Section

In the preparation of PPO, the catalyst is prepared first and then the reactants are added.<sup>8</sup> In a typical catalyst preparation, 1.23 g of  $\text{CuBr}_2$  is stirred in 15 mL of MeOH. The mixture is then transferred to a 3-L flask containing 1.35 L of toluene and 32.7 g of dibutylamine. The mixture is stirred vigorously with a magnetic stirrer. Compressed air is introduced at a flow rate of 3.7 L/min near the bottom of the flask. Then, over a period of 15 min, the reactants (a solution of 210 g of 2,6-dimethylphenol in 210 g of toluene) are added. The reaction is stopped by shutting off the air flow and adding 200 mL of 50% aqueous acetic acid. The mixture is then transferred to a 3-L separatory funnel, and the toluene layer is separated. The latter is poured into 3.6 L of MeOH and the product precipitates. The product is filtered and then dried at 60  $^\circ\text{C}$  under vacuum. The molecular weight as measured by the  $T_g$  is controlled by the duration of the reaction. After 5 h of reaction the  $T_g$  of the product was 130.9  $^\circ\text{C}$  and the yield was 20%. After 12 h, the  $T_g$  was 211  $^\circ\text{C}$  and the yield 90%.

$^{13}\text{C}$  NMR spectra were recorded at 90.56 MHz with a Nicolet NT-360 WB NMR spectrometer operating at 24  $^\circ\text{C}$  in the Fourier transform mode. The tip angle was 70 $^\circ$ . Low-power, broad-

band proton noise decoupling was used. At least 2000 FIDs were acquired with an acquisition time of 0.4 s and 16K points. Before Fourier transformation, the FID was multiplied with an exponential function to give a line broadening of 1 Hz and zero-filled to 64K. The relaxation time  $T_1$  of the carbons bonded to oxygen was estimated to be 1.4 s from partially relaxed spectra. Therefore, a delay time of 5 s was used. Integrated areas were obtained by curve fitting with the NMCCAP routine supplied by the instrument manufacturer. Chemical shifts are referred to tetramethylsilane by using the central peak of the solvent (deuteriochloroform) resonance as an internal reference at 77.0 ppm.

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## References and Notes

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**Registry No.** PPO (SRU), 24938-67-8; PPO (copolymer), 25134-01-4.