

# Compositional Determination of 2,6-Dimethyl-1,4-phenylene Oxide and Styrene Homopolymer Blends by Infrared Spectrometry and Pyrolysis Gas Chromatography

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## Synopsis

Compositional analysis of 2,6-dimethyl-1,4-phenylene oxide (PPO) and styrene homopolymer blends was accomplished using infrared spectrometry and pyrolysis gas chromatography. In infrared measurements the  $1030/700\text{ cm}^{-1}$  absorption ratio provides percent PPO in the blends within  $\pm 3\%$  of the actual value but with a  $\sigma$  of  $\pm 10$ . In pyrolysis GC measurements, four peaks resulting from the fragmentation of the PPO molecule have been investigated for quantitation. One of these peaks provides results with  $\pm 2\%$  of the PPO present with a  $\sigma$  of 7 when the percent PPO in the blend is above 20.

## INTRODUCTION

Polyblends are of unusual interest from both the scientific and technological point of view because they form a single phase or solid solution over an entire composition range. A number of compatible pairs are known and of these, the blends of polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) have been subjected to special close scrutiny.<sup>1-9</sup> The system PS-PPO exhibits a single compositionally dependent glass transition when examined by a variety of techniques, including differential scanning calorimetry,<sup>1</sup> dynamic mechanical relaxation,<sup>1-4</sup> and the measurement of dielectric properties.<sup>1-5</sup> In such studies PS and PPO are found to be miscible in all proportions, and all evidence indicates that the pair is compatible at the segmental level. The objective of this investigation is to determine quantitatively the homopolymer ratio in the PS-PPO blends via infrared and pyrolysis gas chromatography.

## EXPERIMENTAL

### Preparation of Blends

Appropriate mixtures of polystyrene (Foster Grant 817D,  $\overline{M}_w = 248,000$ ,  $\overline{M}_n = 94,000$ ) and poly(2,6-dimethyl-1,4-phenylene oxide) (Scientific Polymer Products, Ontario, NY,  $\overline{M}_w = 244,000$ ,  $\overline{M}_n = 32,000$ ) were weighed and dissolved in toluene. The solution was then precipitated by a mixture of methanol and toluene in a 6:1 ratio. The excess solvent was evaporated in a vacuum oven.

### Infrared Measurements

The blends were dissolved in chloroform and cast as film on glass slides. The homopolymers are considered compatible over the entire range of blends. The films were dried at 100°C for 15 min to remove excess solvent. The free films obtained were placed in the sample beam of a Perkin-Elmer 621 infrared spectrophotometer and scanned against air from 2000 to 600  $\text{cm}^{-1}$ . A typical infrared scan is presented in Figure 3.

### Pyrolysis Gas Chromatography Measurements

A Chemical Data System Pyroprobe model 100 was used as the pyrolyzer. Quartz sample tubes 30 mm long and 1 mm i.d. were placed in the platinum-coil heating probe. Pyrolysis conditions were varied until the most reproducible pyrograms were obtained. The optimum operating conditions were interface temperature 150°C, ramp time 0 sec, interval 20 sec, and final temperature 600°C. The ramp indicates rise in temperature in °C/msec. Interval indicates the period for which the final temperature is held.

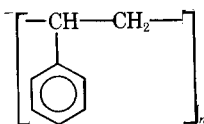
### The Gas Chromatograph

A Hewlett-Packard 5750 chromatograph with 12-ft.  $\times$  1/8-in. stainless steel column packed with 80/100 mesh Chromosorb Q (Applied Science) and coated with 10% W-982 was used. Operating conditions used were helium flow, 20 ml/min; injection port temperature, 150°C; detector temperature, 300°C; flame ionization detector range,  $10^2$  with 4 $\times$  attenuation; oven temperature, initially 50°C for 2 min and after that programmed to rise to 250°C at the rate of 6°C/min. The sample (100 mg) was weighed in a 10-ml volumetric flask and dissolved in 10 ml methylene chloride. Two microliters of this solution were placed at the center of a quartz sample tube and allowed to dry. The sample tube was placed inside the platinum coil of the pyrolysis probe which was then inserted into the heated interface. Before initiating the run, 10 min were allowed for any entrapped air, residual solvent, etc. to escape. A representative pyrogram is presented in Figure 4 for a PS-PPO polyblend of ratio 50:50. A PEP-2 (Perkin-Elmer) data handling system was used to calculate the peak areas.

## RESULTS AND DISCUSSION

### Infrared Spectrometry

The polystyrene



spectrum presented in Figure 1 shows aromatic characteristics in C=C stretch bands at 1610 and 1495  $\text{cm}^{-1}$ . The overtones falling between 2000 and 1700  $\text{cm}^{-1}$

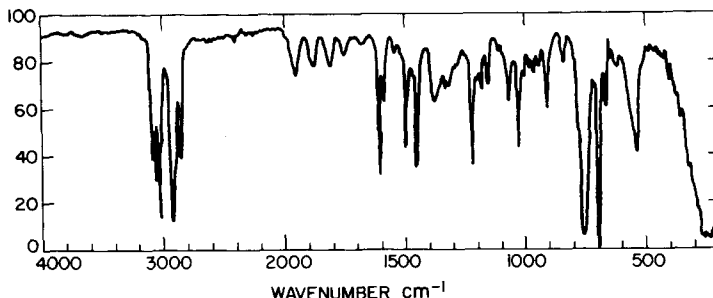
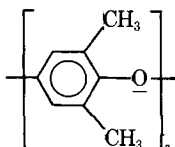


Fig. 1. Infrared spectrum of polystyrene.

indicate monosubstitution of the aromatic ring. The presence of five adjacent hydrogens places their out-of-plane wag vibration band at  $760\text{ cm}^{-1}$ . The band at  $700\text{ cm}^{-1}$ , used for analysis, arises from the ring "puckering" vibration. It is also one of the strongest peaks in the spectrum.

The polyphenylene oxide



spectrum (Fig. 2) also shows the  $\text{C}=\text{C}$  stretch band at  $1610\text{ cm}^{-1}$ , while the band near  $1490\text{ cm}^{-1}$  is merged with the asymmetric deformation vibrations of the methyl groups. The methyl groups show a characteristic symmetric deformation band at  $1380\text{ cm}^{-1}$ . The  $\text{C}-\text{O}-\text{C}$  stretch vibration of an aromatic ether yields the strong band at  $1190\text{ cm}^{-1}$  and is used for analysis. The band at  $1030\text{ cm}^{-1}$ , also used for analysis, is probably related to a ring vibration as it is a feature common to aromatic systems. The tetra substitution (1, 2, 3, 5) provides non-definitive overtones in the  $2000\text{--}1700\text{ cm}^{-1}$  region and places the medium-intensity out-of-plane wag vibration of the hydrogen at  $855\text{ cm}^{-1}$ .

Band ratioing techniques are commonly used in quantitative infrared analysis to eliminate film thickness considerations. According to Beers law,

$$A = atC$$

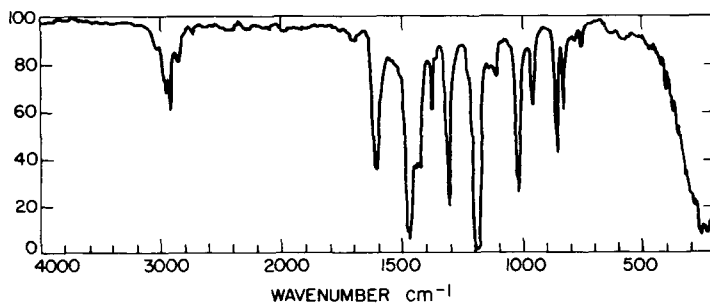


Fig. 2. Infrared spectrum of polyphenylene oxide.

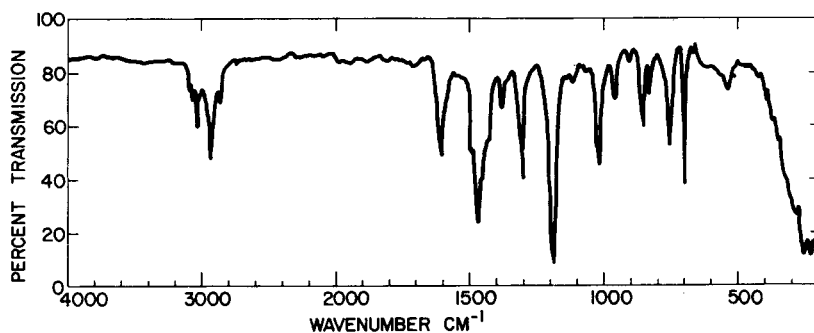


Fig. 3. Infrared spectrum of 50/50 wt % PPO-PS blend.

where  $A$  is absorbance;  $a$ , the absorptivity coefficient;  $t$ , the sample thickness; and  $C$ , the concentration of the absorbing specie. Therefore, absorbances at two different frequencies (i.e.,  $1190\text{ cm}^{-1}$  PPO peak and  $700\text{ cm}^{-1}$  polystyrene peak) can be related as follows:

$$A_{1190} = a_{\text{PPO}} t C_{\text{PPO}}$$

$$A_{700} = a_{\text{PS}} t C_{\text{PS}}$$

$$\frac{A_{1190}}{A_{700}} = \frac{a_{\text{PPO}}}{a_{\text{PS}}} \times \frac{C_{\text{PPO}}}{C_{\text{PS}}}$$

Since  $a_{\text{PPO}}/a_{\text{PS}}$  is constant,  $A_{1190}/A_{700} \propto \% \text{PPO}$ .

A plot of the absorbance ratio ( $1190/700\text{ cm}^{-1}$ ) versus the varying amount of PPO in the blend is presented in Figure 5. The PPO band at  $1030\text{ cm}^{-1}$  is also compared to  $700\text{ cm}^{-1}$  band and the plot is presented in Figure 6. At least five determinations were made for each concentration in these plots, and the range indicates highest and lowest values obtained.

Two samples of 20/80 and 35/65 PPO/PS weight ratios were analyzed, and results are presented in Tables I and II. It is clear that both plots provide results  $\pm 1\%$  of the actual value for the 20/80 sample, for an average of five determinations. However, the  $1030/700\text{ cm}^{-1}$  absorbance ratio provides a larger variation,

TABLE I  
Infrared Analysis of a Sample Containing a Weight Ratio of 20/80 PPO/PS

1190/700 $\text{cm}^{-1}$			1030/700 $\text{cm}^{-1}$		
Absorbance ratio	Weight ratio	% PPO	Absorbance ratio	Weight ratio	% PPO
0.92	0.26	20.8	0.21	0.23	18.7
0.93	0.26	20.9	0.24	0.26	20.6
0.94	0.27	21.0	0.26	0.32	24.2
0.93	0.26	20.9	0.21	0.23	18.7
0.91	0.26	20.8	0.22	0.24	19.4
		Average = 20.9			Average = 20.3
		$\sigma = 0.0837$			$\sigma = 2.3$
		$\sigma\% = 0.4$			$\sigma\% = 11.3$

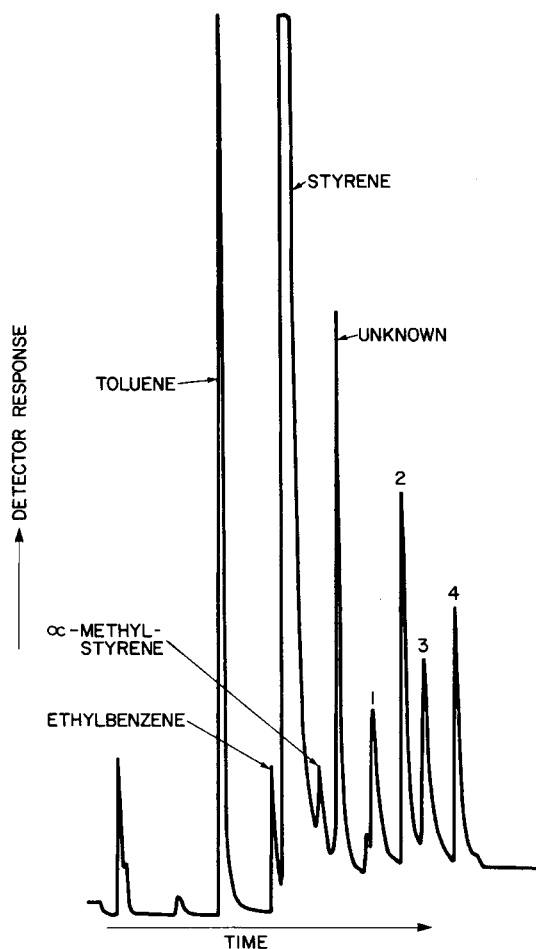


Fig. 4. Pyrolysis gas chromatograph of 50/50 wt % PPO-PS blend.

TABLE II  
Infrared Analysis of a Sample Containing a Weight Ratio of 35/65 PPO/PS

1190/700 $\text{cm}^{-1}$			1030/700 $\text{cm}^{-1}$		
Absorbance ratio	Weight ratio	% PPO	Absorbance ratio	Weight ratio	% PPO
1.59	1.2	54.5	0.33	0.43	30.1
1.67	1.6	61.5	0.31	0.42	29.6
1.47	1.0	50.0	0.33	0.43	30.1
1.60	1.1	52.3	0.41	0.60	37.5
1.51	1.05	51.2	0.36	0.50	33.3
Average = 53.9			Average = 32.12		
$\sigma = 4.56$			$\sigma = 3.35$		
$\sigma\% = 8.46$			$\sigma\% = 10.42$		

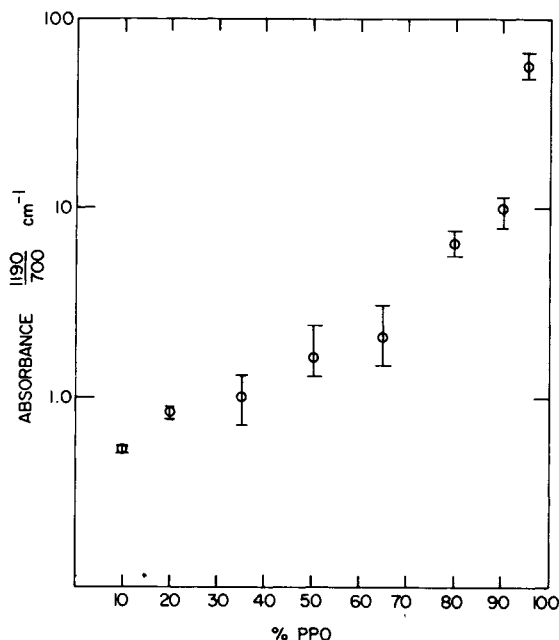


Fig. 5. Plot of absorbance ratio  $1190/700\text{ cm}^{-1}$  vs. wt % PPO in the blend.

as reflected in the value of  $\sigma\%$ . Results for 35/65 PPO/PS weight ratio sample (Table II) provide about 54% higher value using the  $1190/700\text{ cm}^{-1}$  absorbance ratio, whereas the  $1030/700\text{ cm}^{-1}$  ratio provides an average value of 32.12. This is due to the fact that the  $1190/700\text{ cm}^{-1}$  is linear only at lower regions. The  $1030/700\text{ cm}^{-1}$  absorbance ratio provides results within  $\pm 3\%$  of the PPO present and is recommended for analysis.

### Pyrolysis Gas Chromatography

Fragmentation from pyrolysis results in 9–13 components, as seen in a typical

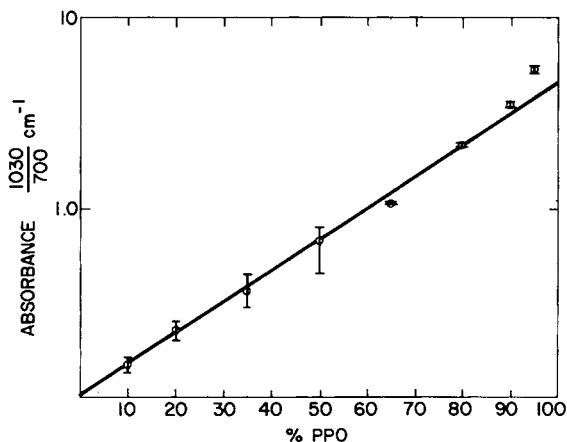


Fig. 6. Plot of absorbance ratio  $1030/700\text{ cm}^{-1}$  vs. wt % PPO in the blend.

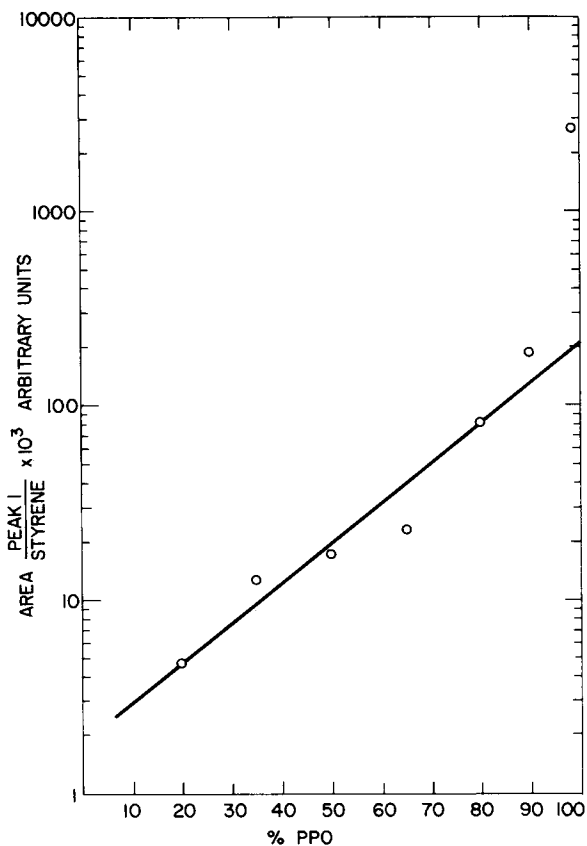


Fig. 7. Area ratio peak 1/styrene vs. wt % PPO in the blend.

TABLE III  
Pyrolysis GC Analysis of a Sample Containing a Weight Ratio of 20/80 PPO/PS

Area peak 1/ area styrene peak	Area peak 2/ area styrene peak	Area peak 3/ area styrene peak	Area peak 4/ area styrene peak
0.01405	0.00421	0.00334	0.00340
0.01679	0.00566	0.00415	0.00500
0.01713	0.00710	0.00581	0.00384
0.01506	0.00568	0.00484	0.00417
0.01307	0.01218	0.00407	0.00277
0.01620	0.00333	0.00413	0.00689
0.01225	0.00341	0.00340	0.00490
0.01565	0.00591	0.00435	0.00648
0.01489	0.00492	0.00469	0.00576
0.01491	0.00459	0.00423	0.00523
Average = 0.01500	Average = 0.00570	Average = 0.00430	Average = 0.00484
% PPO = 44.0	14.3	12.3	20.8
$\sigma$ = 0.00156	0.00256	0.00071	0.00132
$\sigma\%$ = 10.4	44.9	16.5	27.3

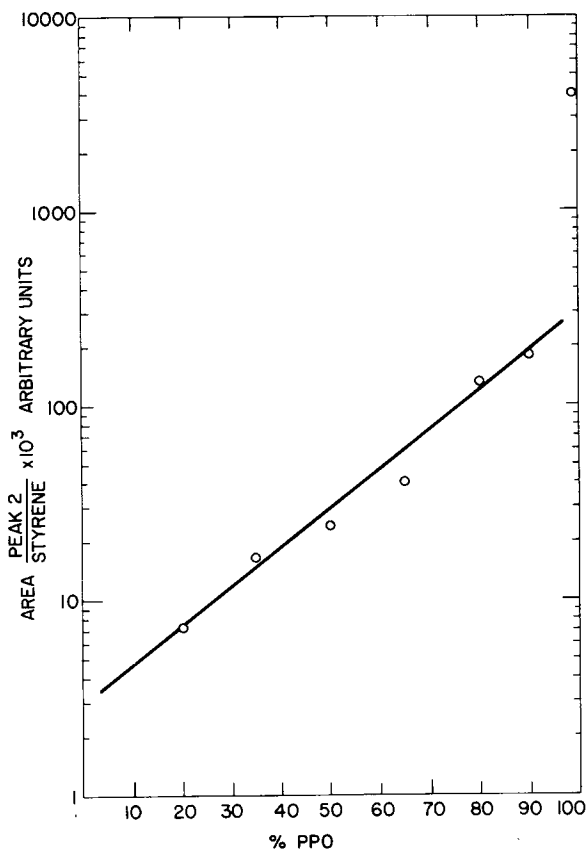


Fig. 8. Area ratio peak 2/styrene vs. wt % PPO in the blend.

TABLE IV  
Pyrolysis GC Analysis of a Sample Containing a Weight Ratio of 35/65 PPO/PS

Area peak 1/ area styrene peak	Area peak 2/ area styrene peak	Area peak 3/ area styrene peak	Area peak 4/ area styrene peak
0.01033	0.01699	0.01281	0.01208
0.01441	0.01487	0.01572	0.01108
0.01334	0.01418	0.01667	0.01096
0.01205	0.01513	0.01597	0.01113
0.01129	0.01588	0.01453	0.01063
0.00728	0.01677	0.01166	0.01144
0.01485	0.01624	0.01215	0.00990
0.01589	0.01815	0.01234	0.01163
0.01502	0.01645	0.01357	0.00983
0.01185	0.01675	0.01377	0.01210
Average = 0.01263	Average = 0.01614	Average = 0.01392	Average = 0.01108
% PPO = 41.0	38.2	38.8	37.0
$\sigma = 0.00262$	0.00116	0.00175	0.00792
$\sigma\% = 20.7$	7.2	12.5	7.1



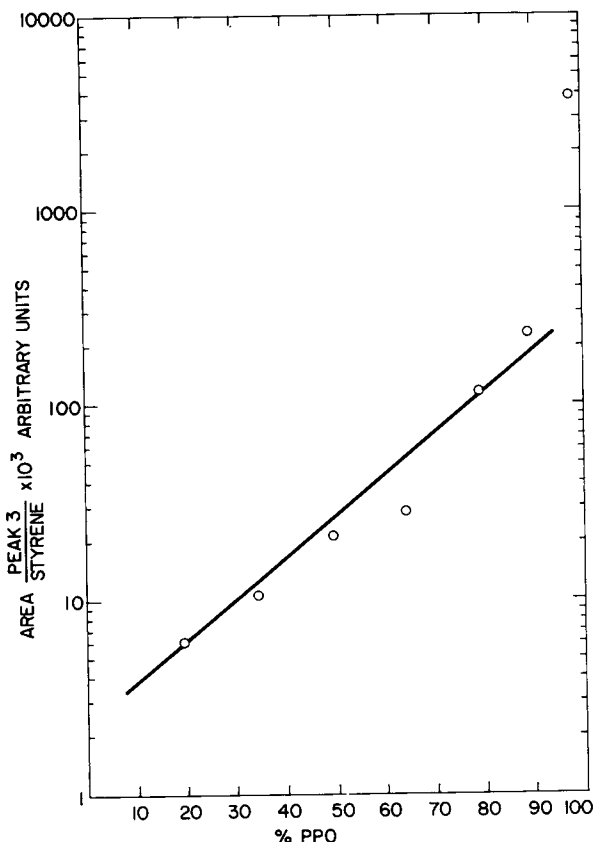


Fig. 9. Area ratio peak 3/styrene vs. wt % in the blend.

GC scan (Fig. 4). Of these, four can be assigned to styrene, toluene, ethylbenzene, and  $\alpha$ -methylstyrene. The latter three molecules are always associated with styrene. The peak labeled unknown decreases in area as the styrene percentage decreases in the blend. This leads us to think that the unknown component is either associated with or results from the fragmentation of styrene. Peaks labeled 1, 2, 3, and 4 are fragments from phenylene oxide in the blend. Ratio of each of the peak areas to the peak area of styrene versus percent PPO is plotted in Figures 7–10. Peak 4 shows greatest linearity. It is difficult to explain as to why peaks 1, 2, and 3 show a departure from linearity. One can only speculate that concentration of the fragment obtained from the rearrangement and scission mechanism of the polymer backbone is not uniform with varying concentration of PPO. All the results indicate that the recommended range for the analysis is between 20 and 80% PPO in the PPO/PS blends by pyrolysis GC.

Jachowicz and co-workers<sup>10</sup> studied the decomposition of poly(2,6-dimethyl-1,4-phenylene oxide) under vacuum and contend that the first degradation step is the Fries-type rearrangement reaction during which the ether bond in the backbone is replaced by a C–C bond according to the following scheme:

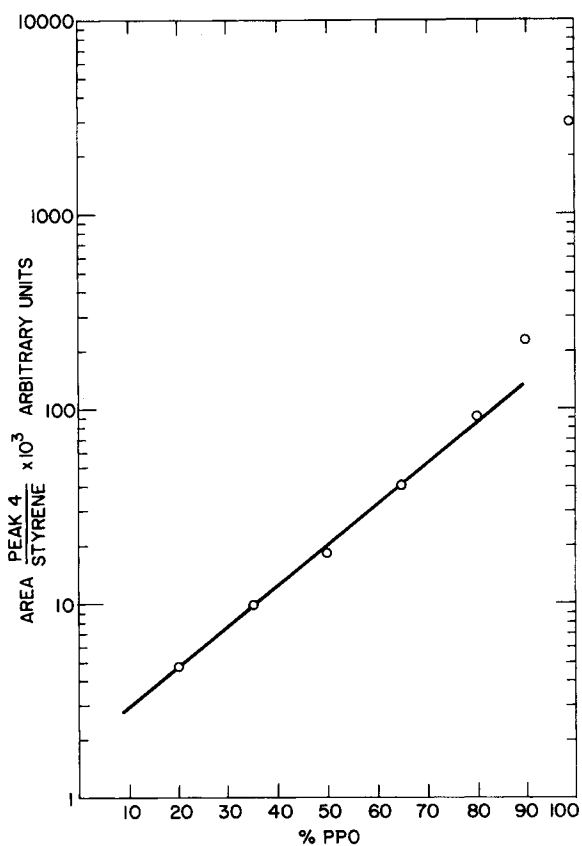
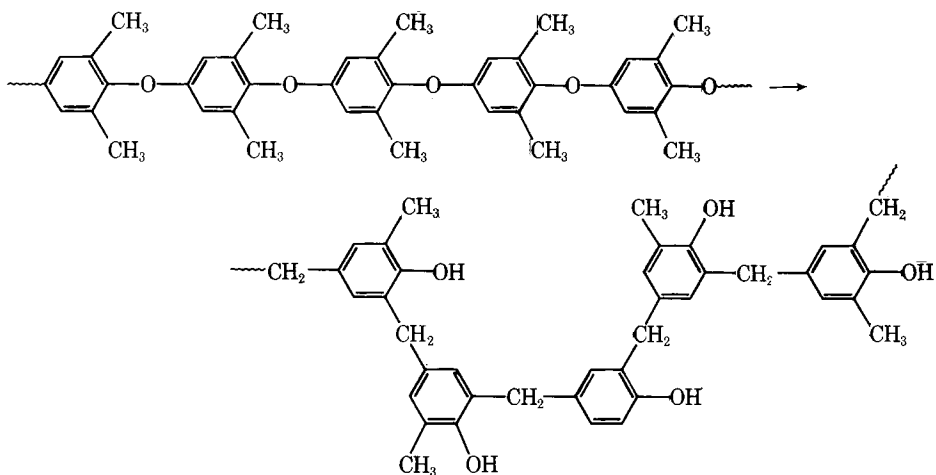


Fig. 10. Area ratio peak 4/styrene vs. wt % PPO in the blend.

The rearranged polymer backbone then decomposes by statistical scission of the C-C bonds forming monomeric and dimeric phenols ranging in the molecular weight of 108 to 256.

Pyrolysis GC results for 10 analyses of the 20/80 PPO/PS sample are presented

in Table III. The area ratios of peak 4 and the styrene peak provide results within 10% of the PPO present. The  $\sigma\%$ , however, is 27.3. For the 35/65 sample, areas for peaks 2, 3, and 4 provide results between 2 and 6% of PPO present (Table IV). Peak 4, however, provides the greatest precision and accuracy above 20% PPO. For best results this peak should be used for a 20 to 80% PPO range in the blend.

In conclusion, both the infrared and pyrolysis GC measurements can be used for a rapid analysis of PPO/PS blends in the range of 20 to 80% PPO. Infrared measurements using 1030/700  $\text{cm}^{-1}$  ratio provide results within  $\pm 3\%$  of the PPO present but with a  $\sigma\%$  of about 10. Pyrolysis GC measurements using peak 4 provide results with  $\pm 2\%$  of the PPO present and a  $\sigma\%$  of 7 above 20% PPO in the blend.

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