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Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Chander, Kunal , Anand, R. C. and Varma, Indra K.(1983) 'Modification of Poly(2, 6-dimethyl-1,4-phenylene Oxide): Phosphorylation Studies', Journal of Macromolecular Science, Part A, 20: 7, 697 — 709

To link to this Article: DOI: 10.1080/00222338308061802

URL: http://dx.doi.org/10.1080/00222338308061802

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J. MACROMOL. SCI.-CHEM., A20(7), pp. 697-709 (1983)

Modification of Poly(2,6-dimethyl-1,4-phenylene Oxide): Phosphorylation Studies

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ABSTRACT

Side chain bromination of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was carried out by using N-bromosuccinimide followed by phosphorylation of the bromo derivative with triethyl phosphite. Optimum conditions for minimum gel formation have been established. The products have been characterized by ^{1}H-NMR and IR studies. Thermal behavior was investigated by thermogravimetry and differential scanning calorimetry in an air/nitrogen atmosphere. Phosphorylated PPO starts to lose weight at 200°C, but the char yield increases with an increase in the phosphorus content of the polymer.

INTRODUCTION

Phosphorus-containing compounds have been used as nondiscoloring stabilizers for various polymeric materials [1]. Esters of phosphorus acids (alkyl and aryl phosphites) and polyphosphites are of particular interest and have been used as stabilizers for raw and vulcanized rub-

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0022-233X/83/2007-0697$3.50/0

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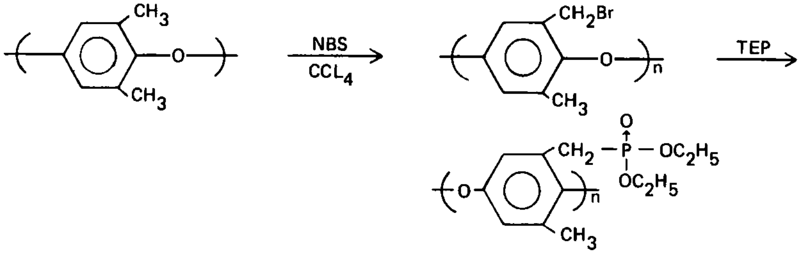
ber, polyolefins, PVC, phenol-formaldehyde polymers, and poly(ethylene terephthalate) [2]. The use of zinc di-n-hexyl dithiophosphate for enhancing the photooxidative degradation of poly(2,6-dimethyl-1,4-phenylene oxide) has been reported recently [3].

The difficulty with low molecular weight stabilizers is their tendency to leach out. Polymers having phosphorus as an integral part of the backbone may be more stable for thermooxidative degradation. The modification of commercially available polymers by reaction with phosphorylating agents has been successfully used in several cases [4-6]. We now report the modification of poly(2,6-dimethyl-1,4-phenylene oxide) by introduction of phosphonate group as shown by the following reaction sequence:



In this paper the synthesis, characterization, and thermal behavior of polymers is described. The aim of these investigations is to use these modified polymers as stabilizers for polyolefins, nylon 6, and other commercially available polymers. These studies will be reported in subsequent papers.

EXPERIMENTAL

2,6-Dimethylphenol (Fluka) was crystallized from hexane. Nitrobenzene (BDH) was distilled and the middle fraction (bp 85°/10 mm) was collected. Cuprous chloride was freshly prepared in the laboratory from $CuSO_4$ and NaCl (both from BDH) according to a method reported in Vogel [7]. Freshly crystallized N-bromosuccinimide (NBS) (BDH) and double distilled triethyl phosphite (TEP) (bp 156°) were used. Diglyme was kept over CaH_2 for a week followed by distillation (bp 162°). Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), obtained from General Electric Co., had $[\eta]^{30}_{CHCl_3} = 0.42$ dL/g and $\overline{M}_n$ 28,500. This commercial sample has been designated as "S" (Table 1).

Preparation of Poly(2,6-dimethyl-1,4-phenylene Oxide) (PPO)

PPO was prepared according to the method of Hay et al. [8] by bubbling O_2 through a solution of pyridine (12 mL), nitrobenzene (34

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TABLE 1. Characterization of Various PPO Samples and Substituted PPO Samples

No.	Sample no.	$[\eta]$ (dL/g)	K' (Huggins') constant
1	S	0.42	0.5
2	A	0.15	-
3	B	0.33	1.9
4	C	0.40	0.89
5	D	0.63	0.45
6	E	1.05	2.63
7	F	1.70	0.39
8	G	1.93	0.65
9	H	2.0	3.55
10	S_1	0.21	0.88
11	C_1	0.21	-
12	S_2	0.17	2.42
13	C_2	0.216	3.3
14	C_2 *	0.265	2.8

mL), and cuprous chloride (0.167 g), and then adding 2,6-xylenol (2.5 g) with stirring at 30°C. After 0.5 h it was worked up by diluting with chloroform (20 mL) and then adding CH_3OH (200 mL) containing conc HCl (0.5 mL). The polymer was filtered and then purified by reprecipitation (three times) from a $CHCl_3$ solution using CH_3OH as nonsolvent. After washing with CH_3OH the precipitated polymer was dried in a vacuum oven at 70°C.

Different samples (A-D) were prepared by changing the duration of the reaction. The intrinsic viscosities of various polymers are given in Table 1.

In the above procedure, use of dried cuprous chloride resulted in the formation of yellow-colored PPO. Again, by varying the reaction time, different samples (E-H) were obtained. However, no additional bands were noted in the IR spectra of these colored samples. The intrinsic viscosities are given in Table 1.

Bromination of Poly(2,6-dimethyl-1,4-phenylene Oxide)

Samples S and C of PPO were brominated in batches of 7 g in CCl_4 (1.5 L), NBS (10.8 g), and benzoyl peroxide (0.1 g) according to the procedure reported in the literature [9]. The bromo derivatives, poly(2-bromomethyl-6-methyl-1,4-phenylene oxide) (designated S_1 and C_1, respectively) were obtained in 95 and 96% yields, respectively (Table 1).

Phosphorylation of Poly(2-bromomethyl-6-methyl-1,4-phenylene Oxide)

Method I

A mixture of poly(2-bromomethyl-6-methyl-1,4-phenylene oxide) and TEP was stirred and refluxed for 3.5 h. It was cooled and filtered to remove any gel. Excess TEP was distilled off and the residue was triturated with cold water several times. Water was decanted off and the residue was dried. Reprecipitation of the phosphorylated polymer from CH_3OH by distilled water (three times) gave the desired polymer which was dried under vacuum at 70°C for 2 d. Phosphorylated polymers were prepared from commercial PPO and Sample C. These have been designated as S_2 and C_2, respectively (Table 1).

Method II

To a refluxing mixture of TEP (20 mL) and diglyme (20 mL) was added C_1 (10 mL, 5% solution in diglyme) dropwise with stirring. After refluxing for 4 h it was worked up as described in Method I to afford phosphorylated polymer C_2* in 90% yield.

Characterization

Intrinsic viscosity measurements were carried out at 30°C in $CHCl_3$ using an Ubbelohde viscometer.

PMR spectra were recorded using $CDCl_3$ or CCl_4 as solvents and trimethylsilane as the internal standard on a Perkin-Elmer Model Spectrometer. IR spectra were recorded in KBr pellets or as a liquid film on a Pye Unicam SP 1200. Bromine estimation was carried out by a modified Stepanow's method [10]. For example, the NaBr solution, prepared by refluxing bromo-PPO (0.05 to 0.75 g) with Na (0.5 to 0.62 g) in monoethanolamine (6 mL) and dioxane (3 mL), was treated with an excess of 0.05 N $AgNO_3$ solution. The unreacted Ag^+ ions were estimated by titrating against 0.05 N KCNS.

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Phosphorus Estimation

Phosphorylated PPO (0.15 to 0.25 g) was digested in conc H_2SO_4 (12.5 mL) and $HClO_4$ (14 mL). To this solution, after neutralization with NH_3, was added conc HNO_3 (10 mL) and solid NH_4NO_3 (10 g). The temperature of the solution was raised to 75-80°C and then ammonium molybdate solution was added in excess. The precipitate was filtered, washed with NH_4NO_3 solution (2%) followed by distilled water repeatedly till it is neutral to litmus. The precipitate was dried at 120°C for 6 h to constant weight.

Thermal Behavior

A Du Pont 990 Thermal Analyzer was used for evaluating the thermal behavior of the polymers. Finely powdered (5 to 15 g) samples were heated under static air or an N_2 atmosphere at 100 cm^3/min.

A Du Pont DSC was used to study the transitions in various polymers. The samples were heated in an aluminum pan at a rate of 10°C/min in static air or an N_2 atmosphere.

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RESULTS AND DISCUSSION

Phosphorylation of PPO was carried out through Arbuzov's reaction by refluxing the bromo-PPO (S_1 and C_1) with TEP. This reaction is normally accompanied by gel formation [5]. Cabasso et al. have reduced gelation by carrying out the reaction in diethylcarbitol [5]. In the present investigations we have observed that gelation is dependent upon 1) the concentration of TEP, 2) the initial rate of heating, and 3) stirring during the reaction. The optimum conditions which completely eliminate gel formation are a large excess of TEP, vigorous stirring, and a slow rate of initial heating (Table 2).

Characterization

The yellow-colored polymers E to H could not be decolored by a charcoal treatment or by continuous extraction by various solvents. Although these polymers show very high intrinsic viscosities, yet $\overline{M}_n$ (from HPLC) is fairly low. This could be attributed to association in polymer solution which increases the flux time.

Bromo PPO shows lower $[\eta]$ than the corresponding phosphorylated PPO. This may be due to the introduction of bulkier groups in the side chains of phosphorus-containing polymers.

TABLE 2. Effect of TEP[a] on Gel Formation During Phosphorylation

No.	Amount of TEP (mL)	Phosphorous content (%)	Amount of gel (mg)	Yield (%)
1	70	8.2	0	92
2	65	10	20	91
3	50	10	100	90
4	30	10	200	90

[a] 1 g of C_1 sample was used in all these experiments.

PMR and IR

PMR spectral data is in good agreement with the structure of phosphorylated PPO. A doublet around δ3.1 (2H, J = 20 Hz) is due to the $-CH_2-P$ group. The presence of $-P'(O-CH_2-CH_3)_2$ has been shown by a triplet at δ1.2 (6H, J = 7 Hz) and a multiplet at δ4.0 (4H). Aromatics methyl and aromatic protons appear at δ2.1 (s, 3H, CH_3-Ph-) and δ6.6 (m, 2H), respectively (Fig. 1). In IR spectra, P=O stretching vibrations appear at 1270 cm^{-1}. A sharp band at 780 cm^{-1} has been assigned to phosphorus benzyl stretching vibrations (Fig. 2).

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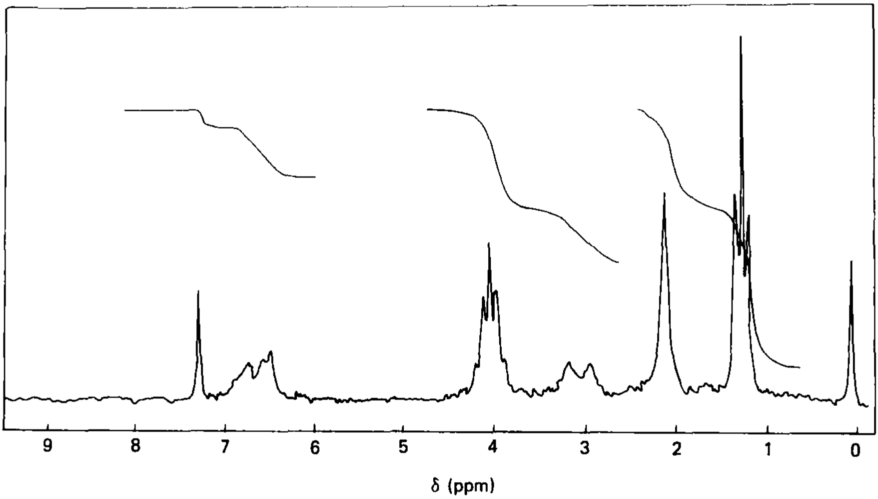

FIG. 1. ^{1}H-NMR spectrum of phosphorylated poly(phenylene oxide) in $CDCl_3$.

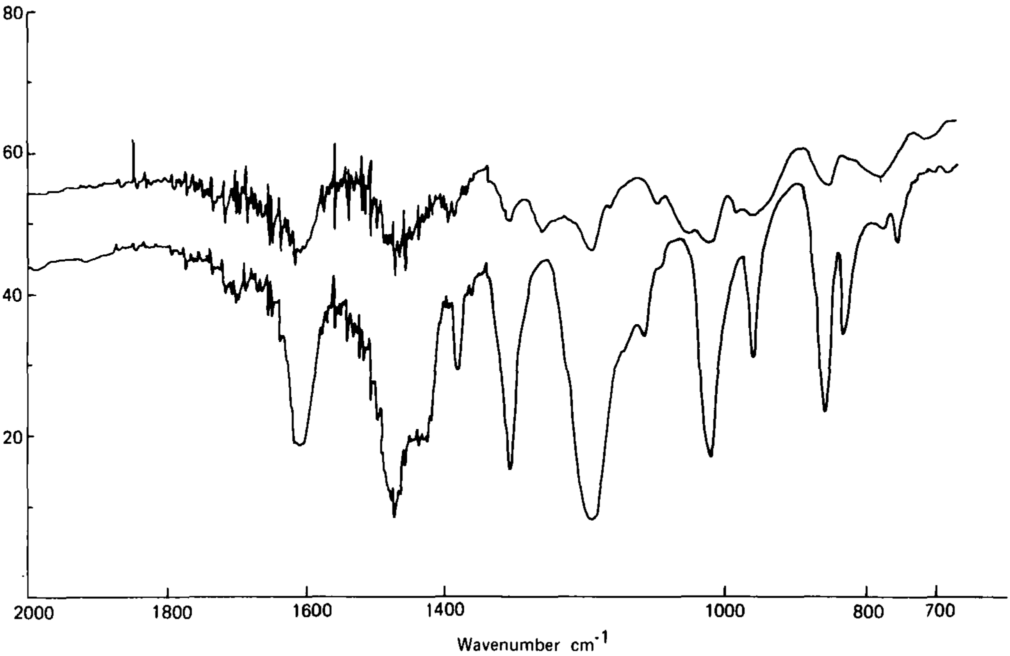

FIG. 2. IR spectra of (bottom) poly(phenylene oxide) and (top) phosphorylated poly(phenylene oxide).

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THERMAL BEHAVIOR

Differential scanning calorimetry was studied in an air atmosphere. Sample C_2 showed three endothermic peaks (Fig. 3). The first endotherm at 186°C may be attributed to T_m. In the cooling curve of sample C_2, an exotherm was observed at 171°C which is due to crystallization. The other two endothermic peaks are accompanied by weight loss and may be due to a degradation reaction [5].

The effect of intrinsic viscosity/molecular weight and atmosphere on the thermal behavior of polyphenylene oxide samples was investigated by thermogravimetry. From the thermogravimetric traces, initial decomposition (PDT) and final decomposition temperatures were obtained by an extrapolation method (Table 3). The integral procedural decomposition temperature (IPDT) was calculated in the temperature range of 25 to 800°C in a nitrogen atmosphere [11]. The temperature of maximum rate of weight loss (T_{max}) was obtained from a plot of dw/dt vs temperature.

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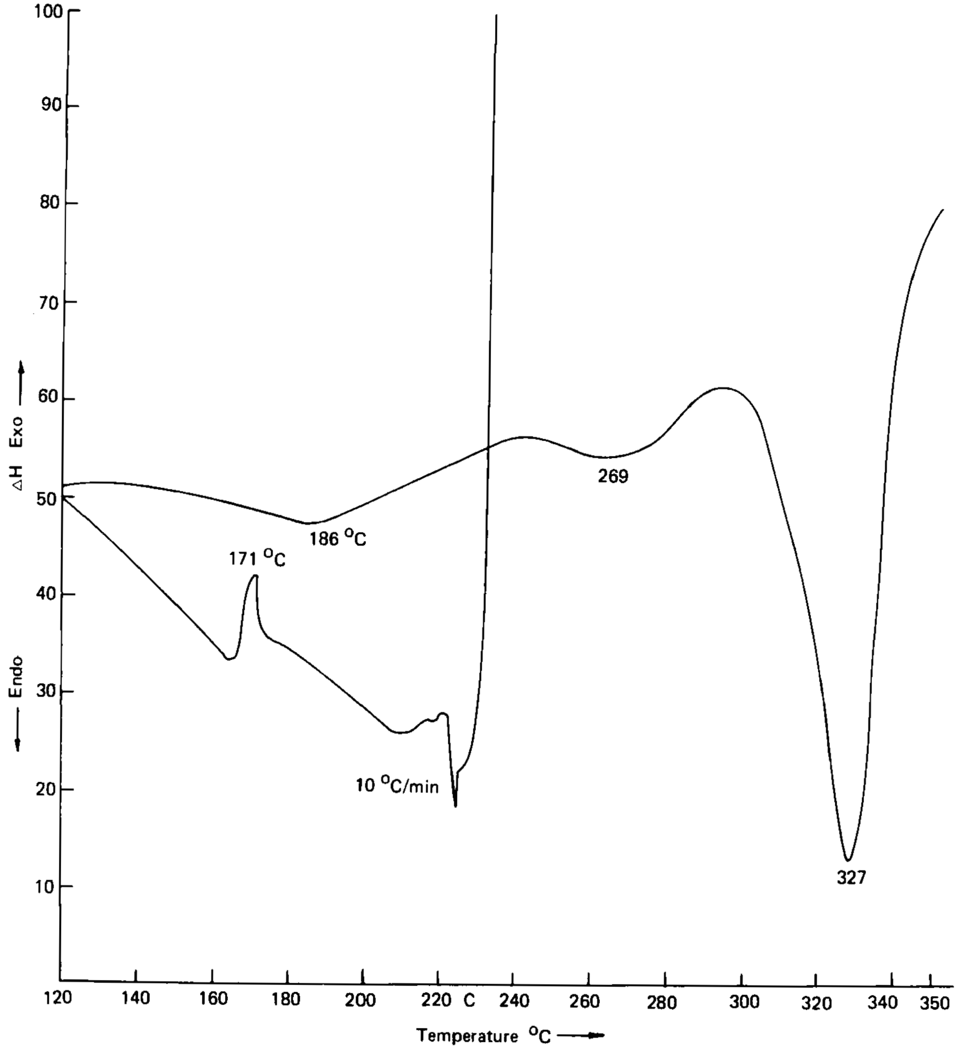

FIG. 3. DSC traces for Sample C_2 (top curve) and cooling curve for Sample C_2 (bottom curve).

TABLE 3. Thermal Behavior of Various PPO Samples in Air and Nitrogen Atmosphere

No.	Sample	$[\eta]$ dL/g	PDT[a]	IPDT[b]	T_{max}	T_f
1	A	0.15	430	606	460	475
2	C	0.40	420	600	490	470
			(350)	(483)	(490, 505)	(600)
3	F	1.70	360	577	555	700
			(340)	(458)	(490)	(505)
4	H	2.0	360	-	550	620
			(345)	(443)	(500)	(530)
5	C[c]	0.8	425	606	455	650
			(360)	(467)	(475, 545)	(615)

[a] Values in parenthesis indicate the corresponding decomposition temperature in air.

[b] IPDT values are calculated when T_i is in the range of 25 to 800°C (N_2 atmosphere) and 25 to 500°C (air).

[c] This PPO sample was obtained from Sample C by fractionation.

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Poly(phenylene oxide) samples were stable in air and nitrogen atmospheres up to 350°C and started decomposing above this temperature. PDT values were lower in an air atmosphere, and two T_{max} were observed in Sample C. An increase in molecular weight of samples resulted in a slight decrease in PDT and IPDT. However, an increase in T_{max} was observed (Table 3). Sample C was fractionated by precipitation to obtain a fraction of higher intrinsic viscosity C*. The T_f of this sample was considerably higher. From these results it may be concluded that the onset of thermal degradation in poly(phenylene oxide) is not dependent on the molecular weight of the samples. However, if some impurities are present (as in yellow-colored Samples E to H), then degradation is initiated at a low temperature. The IPDT of commercial polymer Sample S was lower than that of Sample C (Table 4).

The effect of substitution of hydrogen for the methyl group of PPO by bromine or phosphorylation, on thermal behavior of poly(phenylene oxides), was also evaluated (Figs. 4 and 5). A considerable reduction in PDT and IPDT was noticed by bromination (C_1), even though the char yield at 800°C was not affected. Phosphorylated samples

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TABLE 4. Thermal Behavior of Substituted PPO in a Nitrogen Atmosphere

Sample	$[\eta]$ (dL/g)	PDT (°C)	Temperature at various % residual weight (°C)					IPDT (°C)	Char yield (%)[a]
			10%	20%	30%	40%	50%		
S	0.42	430	450	455	460	465	470	573	28
C	0.40	420	430	450	460	470	520	600	37
C_1	0.21	250	290	310	330	450	550	557	38
S_2	0.17	230	320	350	490	650	-	634	55
C_2	0.21	200	320	345	470	480	500	577	40
C_2 *	0.26	200	320	340	480	490	550	591	44

[a] Char yield was calculated at 800°C.

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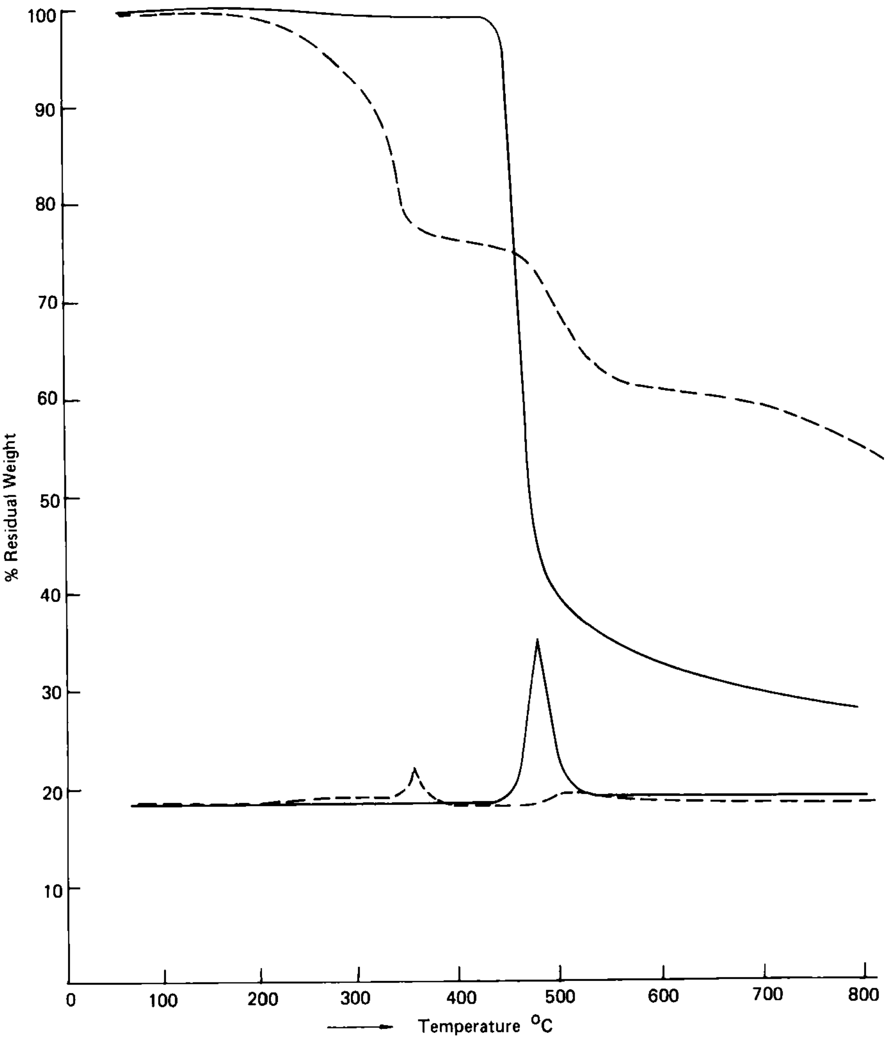

FIG. 4. Thermogravimetric traces of commercial poly(phenylene oxide) (S) (—) and phosphorylated poly(phenylene oxide) (S_2) (- -) in nitrogen atmosphere.

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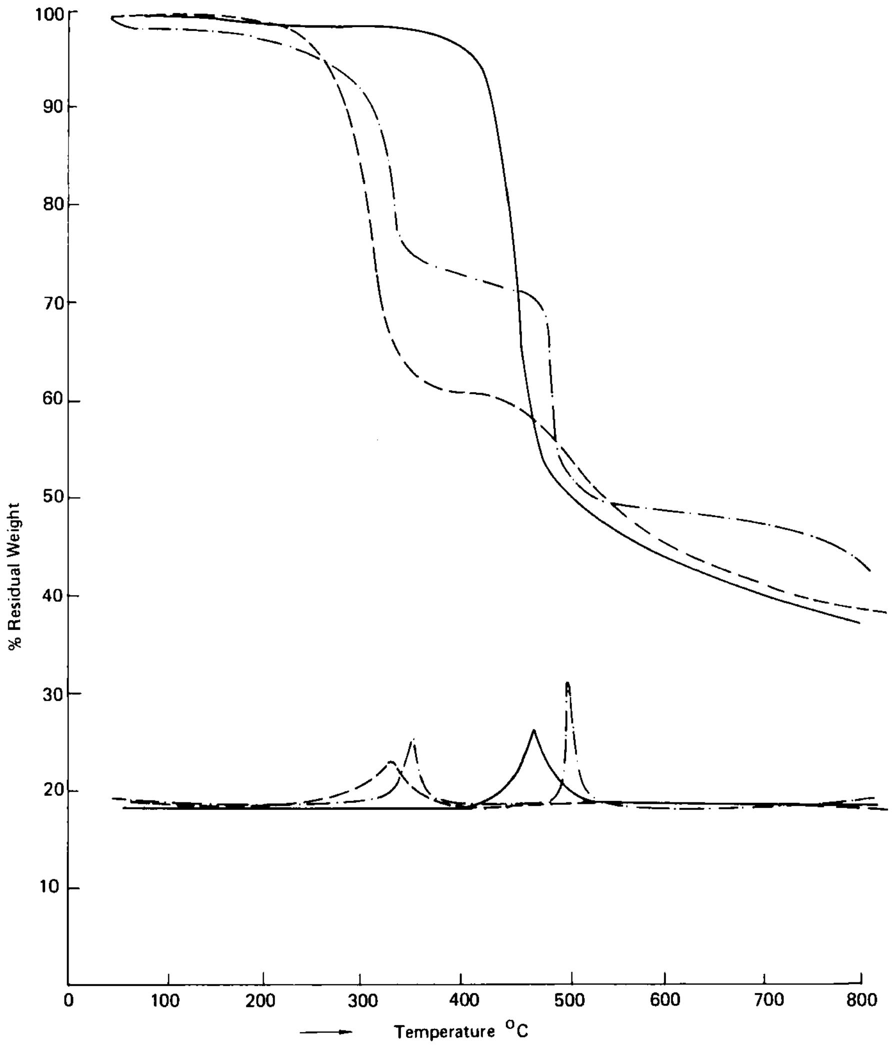

FIG. 5. Thermogravimetric traces of poly(phenylene oxide) (C) (—), bromo poly(phenylene oxide) (C_1) (- -), and phosphorylated poly(phenylene oxide) (C_2 *) (- • -).

showed a two-step decomposition behavior and char yields were much higher (40-55%). These results clearly indicate that phosphorylation increases the condensed phase reaction, thus increasing the char yield of the residue.

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Accepted by editor June 6, 1983
Received for publication July 8, 1983

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