Pyrolysis of polystyrene–poly(2,6-dimethyl-1,4 phenyleneoxide) mixtures and graft copolymers

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The influence of poly(2,6-dimethyl-1,4-phenyleneoxide) [PPO] on the thermal degradation of polystyrene [PS] has been investigated over the whole range of admixed homopolymer contents and for selected compositions of grafted copolymers of PS chains on PPO. The styrene yield on pyrolysis at 350–650°C was measured. The results are discussed in terms of the miscibility of the system and its influence on the course of pyrolysis, i.e., on participation of competitive processes in the overall mechanism of PS degradation. On the basis of the data, regression equations for the dependence of styrene concentration on the composition of the mixture were determined and the results show that the styrene content at pyrolysis near 500°C does not depend on the molecular interaction of the PS–PPO system. It is demonstrated that pyrolysis and gas chromatography can be used for determination of the composition of polymer mixtures and of copolymers.

INTRODUCTION

Investigations on the yields of individual products of pyrolysis from various polymers have demonstrated their dependence on the process temperature, the rate of host input and on the mass and dimensions of the sample[1–5]. These relations arise from different mechanisms of degradation and different contributions of individual components in the processes, which should be taken into consideration in a general kinetic scheme describing thermal degradation. Quantitative investigation of the products of very rapid degradation (thermolysis at high temperature or photolysis) showed the dependence of the nature of the products on the relative rate of the reactions and on diffusion processes such as monomer evolution from the bulk of the sample.

Investigations of the mechanism of thermal degradation of polystyrene[6–8] indicate that the most important process is that of unzipping, accompanied by simultaneous intra- and intermolecular transfer by hydrogen abstraction.

The process of depolymerization, which most authors suggest[2,7,8], is initiated at the end of a chain, with intramolecular hydrogen transfer leading to the formation of degradation products other than monomer. Styrene is formed only in the unzipping process.

Investigations of the products of pyrolysis of polystyrene in an inert atmosphere and in a vacuum have been the subject of numerous papers and monographs[1,2]. Two ranges of thermal degration of polystyrene were established; the first one below 300°C, the other above that temperature. In thermal degradation below 300°C a considerable reduction in the molecular weight of polystyrene is observed and simultaneously oligomeric products are formed. At higher temperatures, however, the degradation process occurs with increased yield of volatile products ($\sim 65\%$) which are mostly monomer, and smaller amounts of oligomeric compounds.

Investigations on the thermal degradation of polystyrene mixtures in homogeneous[9] and heterogeneous[10] systems have indicated the large influence of the mixture components on the yield of styrene in the pyrolysis products. The authors of the latter work showed that in polystyrene–poly(α-methylstyrene) mixtures the latter polymer, which is less stable than polystyrene, depolymerized almost completely to monomer at a temperature $\sim 50°C$ lower than polystyrene and formed monomeric radicals capable of initiating the depolymerization of polystyrene.

Poly(2,6-dimethyl-1,4-phenyleneoxide) [PPO] is more resistant to thermal degradation than is polystyrene[11]. The degradation process of the polymer is statistical with a maximal decrease in mass at a temperature about 50°C higher than for polystyrene. The amount of volatile products from PPO pyrolysis is small ($\sim 40\%$) and the major decomposition product is toluene.

Investigations of the mechanism of thermal degradation in vacuum of polystyrene–poly(2,6-dimethyl-1,4-phenyleneoxide) mixtures[12] show the influence of the components of the system on its course, by limiting intramolecular hydrogen transfer reaction in polystyrene. Examination of the oligomeric products of degradation by mass spectrometry should yield some information on the relative probabilities of the competitive reactions but the interpretation is not conclusive.

At low degradation temperatures and/or at low rate of

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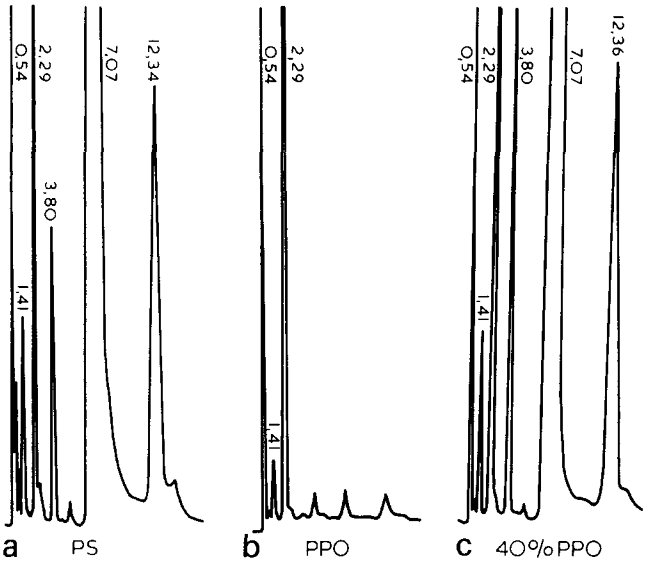


Figure 1 **Chromatograms of pyrolysis products at 500°C (a), for polystyrene; (b), for poly(2,6-dimethyl-1,4-phenyleneoxide); (c), for mixture of 60 wt % of PS**

heating some reactions may lead to the stabilization of polymer since the hydrogen transfer leading to termination of the PS degradation reaction dominates the degradation processes.

Because of the considerable importance of diffusion processes in determining the character and mechanism of degradation, interaction of the components of these complex systems is only possible if they are miscible.

The PS–PPO mixtures examined by us are usually considered to be homogenous. This conclusion follows from investigations on thermal porperties[11] and application of other methods of miscibility investigations[13,14]. Investigation of the permeability of gases through PS and PPO foils[11] showed good miscibility of the components and their strong interaction in the mixture, with possible formation of areas of differing homogeneity resulting in lowering of gas diffusion coefficients for certain compositions of the mixture (40–60% PS). These conclusions concerning the probability of occurrence of microdomain structures are not supported by other investigative techniques.

Our previous investigations of photooxidation processes in PS–PPO mixtures[15] showed the great influence of the components of the system on the course of the processes, especially over the range 40–60% PS.

Because of the great importance of degradation mechanisms and diffusion processes on pyrolysis it seemed interesting to examine the influence of mixture composition and pyrolysis temperature on the yield of the monomer being formed.

Investigations of the pyrolysis products of copolymers[6,17] show the importance of the influence of copolymer microstructure on their quantity. The yield of product depends on the probability of the appearance of different 'mers' in a copolymer chain. Quantitative analysis of pyrolysis products of styrene–butadiene copolymer[18,19] showed considerable differences in the results obtained for statistical, block copolymers and mixtures. The results for block copolymer were closer to those obtained for mixtures.

Pyrolytic gas-chromatography (p.g.c.) is the analytical method used for examination of the concentration of the components in polymer mixtures and in copolymers but does not always lead to satisfactory results.

In order to determine the composition of a mixture of polymers or of copolymer composition by p.g.c. the concentration of the basic product of a mixture or copolymer degradation (usually of one monomer with which the highest peak may be correlated) was examined[20–24]. Chromatographic peak area per unit mass (e.g. Strassburger *et al.*[21]) or per peak area of the second component (Ferlanto *et al.*[22]) or per the introduced standard are expressed as a function of concentration of the components in a mixture or copolymer. For most systems[20–24] a quadratic regression equation was used to describe the dependence of the basic pyrolysis product yield on the concentration of components in the mixture.

Taking into consideration the previous remarks the second aim of this work was to analyse the possibility of using p.g.c. to determine the composition of PS–PPO mixtures and of the grafted copolymers of PS on PPO as well as examine the influence of pyrolysis temperature on the accuracy of the results of this method.

EXPERIMENTAL

Preparation of polymer samples

Polystyrene and poly(2,6-dimethyl-1,4-phenylene-oxide) samples were purified by dissolution in chloroform and precipitation with methanol. Precipitated polymers were dried in vacuum. Mixtures of a suitable composition were obtained from solution of the two polymers in chloroform. Foils 20 μm thick were prepared by pouring the solutions in chloroform onto smooth surfaces. Copolymers were prepared by grafting of PS on PPO by ionic polymerization[25]. Foils from copolymers and mixtures had the same thickness. The composition of the copolymers was determined by high resolution n.m.r.[25].

Pyrolysis gas chromatography

The foils were pyrolyzed in an electric resistance pyrolyzer of the Jeol type with temperature stabilization to ±1°C. Samples of mass 0.3 mg were introduced into the high temperature area in nickel boats. Pyrolysis products were introduced directly into the chromatographic columns by means of nitrogen carrier gas at a flow rate 38.5 ml/min. Two identical columns with 5% Bentonite 34 + 5% DIDP (diisodecylphtalate) were used. The analyses were carried out under isothermal conditions at 75°C.

The Jeol chromatograph employed for analyses of the gaseous products was equipped with a flame-ionization detector. The content of the pyrolysis products was determined as a ratio of chromatographic peak areas to the mass of the polystyrene in the mixture or in copolymer S_{st} (mm^2/μg PS). The area of the styrene peak was obtained by an electronic integrator taking the mean value from two measurements. The results of the investigations were reproducible within ±5%.

N.m.r. studies

The n.m.r. investigations were carried out at room temperature using deuterated chloroform as solvent and TMS (tetramethylsilane) as a reference. The n.m.r. spectrum for PS–PPO mixtures has two resonance areas: these are aliphatic protons and aromatic protons.

Since it appeared impossible to separate signals of PPO

Table 1 Gaseous products for the pyrolysis of polystyrene, poly(2,6-dimethyl-1,4-phenyleneoxide) and a 60 wt % mixture of PS

	Retention time (min)	Relative content at pyrolysic temperature 500° C (S_x/S_0) %
Polystyrene		
Light gases	0.56	0.7
Benzene	1.41	0.3
Toluene	2.29	3.1
Ethylbenzene	3.80	0.8
Styrene	7.07	89.9
α-Methylstyrene	12.36	3.6
Poly(2,6-dimethyl-1,4-phenyleneoxide)		
Light gases	0.54	29.1
Benzene	1.41	5.6
Toluene	2.29	51.0
Mixture of 60 : 40 wt % PS/PPO		
Light gases	0.54	0.9
Benzene	1.41	0.5
Toluene	2.29	7.6
Ethylbenzene	3.80	2.0
Styrene	7.07	83.1
α-Methylstyrene	12.36	4.8

and PS protons within one of the areas, equation (1) was used to determine the composition from the ratio between the areas of aliphatic and aromatic protons.

$$\frac{J_{\text{aliph.}}}{J_{\text{arom.}}}=\frac{6+3\,m/n}{2+5\,m/n} \tag{1}$$

where m/n is the molar ratio PS/PPO. The error of composition determination of PPO with PS mixtures was ±5%.

RESULTS AND DISCUSSION

Chromatograms obtained at the temperature 500°C for pyrolysis of polystyrene, poly(2,6-dimethyl-1,4-phenyleneoxide) and a mixture of 60 wt% of PS and 40% PPO respectively are presented in *Figure 1*. We observed typical products of PS pyrolysis[26–28], i.e. benzene, toluene, ethylbenzene, styrene and α-methylstyrene. Retention times of the identified pyrolysis products and their relative contributions to the total products S_0 at 500°C are given in *Table 1*.

Analysis of chromatograms of volatile products in the pyrolysis of polystyrene and its mixtures over the temperature range 350°–600°C revealed the presence of styrene amounting to 70–90% of all the gaseous products. Other products, i.e. benzene, toluene, ethylbenzene and α-methylstyene, are but a small proportion of all the gaseous products and result from consecutive reactions in the thermal degradation of monomer at high temperature, in accordance with reference 27 dealing with polystyrene pyrolysis the temperature range 300°–500°C.

Investigations of the quantitative analysis of gaseous products in the pyrolysis of mixtures in the temperature range 623–873K revealed the strong influence of the composition of the mixture on the course of pyrolysis, i.e. on the participation of competitive processes in the overall mechanism of polystyrene degradation in the presence of PPO. The dependence of the gaseous products S_0 on the weight content of PPO in the mixture for pyrolysis at 500°C is of a nonlinear character as shown in *Figure 2*.

The amount of gaseous products is greater in the pyrolysis of mixtures than calculated on proportional contribution of the homopolymers.

Figures 3a, b, c, d present the relation of the amount of the identified products to the mixture composition at 350°C, 450°C, 500°C, 650°C, respectively.

For the temperatures above 400°C deviation of styrene yield from additivity is positive and below that temperature it is negative. Similar deviations from additivity can be observed for the products of consecutive reactions, i.e. benzene, toluene, and α-methylstyrene.

The percentages of styrene and of toluene in the gaseous products as a function of the mixture composition at 500°C are given in *Figure 4*. This shows that in the mixture there is an increase of styrene contribution to the mixture of gaseous products and a simultaneous lowering of toluene percentage. The results of styrene yield expressed as a ratio of the chromatographic peak area to the mass of PS present in the mixture for a number of pyrolysis temperatures within the range 350°–650°C are presented in *Table 2*. The yield of styrene shows a maximum at about 500°C. These data correspond to those obtained by Yasuda[26]. A considerable increase (~20%) of styrene contribution in comparison with PS was noticed in the pyrolysis products of the mixture. The maximum yield of styrene monomer in pyrolysis products of the mixture also appears at lower temperatures (~50°) than for PS alone.

The yield of styrene in pyrolysis products per unit mass of PS increases with the increase of concentration of PPO in a mixture at various pyrolysis temperatures (*Figure 5*). The increase of styrene (per unit mass of PS) is connected also with the increase of styrene (S_{st}) in the gaseous products S_0 at about 500°C (*Table 3* and *Figure 6*). The large increase of styrene percentage in the mixtures

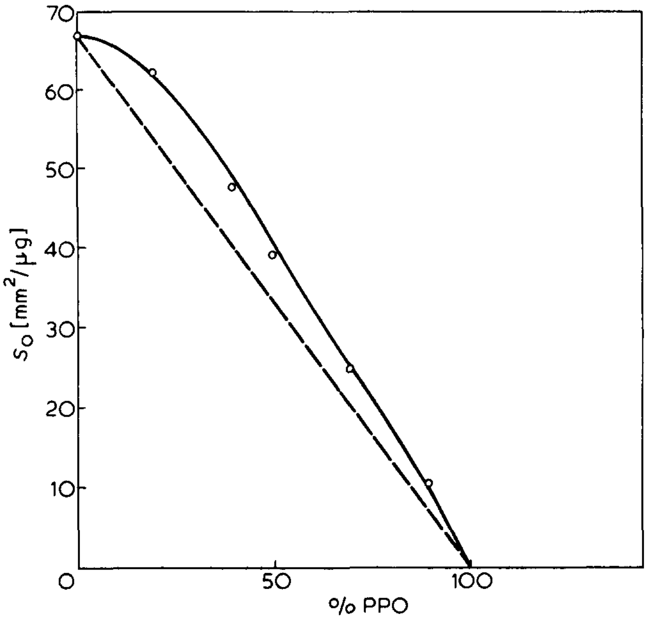
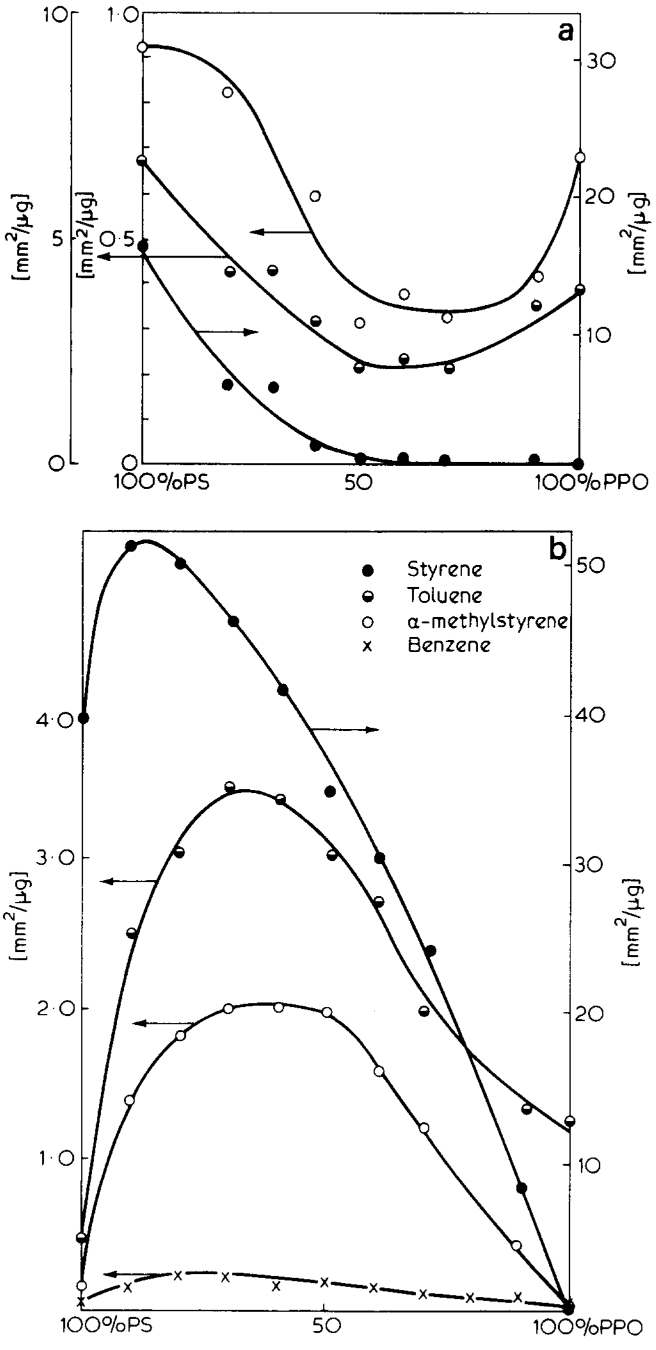


Figure 2 Dependence of total yield of all the gaseous products as a function of weight PPO contribution to PS–PPO mixture pyrolysis at 500°C

reaches a maximum ot 480 C and is related to the drop in toluene percentage (S_T) from the value close to PPO at 300 C to the value close to PS at 450 C (*Table 4* and *Figure 7*). The change in the relative contributions of the two major products in pyrolysis of the mixtures indicate a strong interaction between the components of the mixture during rather fast degradation. These interactions must occur at the molecular level. This conclusion is confirmed by the previous studies on the miscibility of the system[14,15]. The role of the interactions of PS with PPO in a mixture was also confirmed by investigations on copolymers of PPO with grafted PS. The results of the investigations presented in *Table 5* show a difference between the styrene yield for copolymer and mixture of similar composition. Temperature dependences of styrene contribution show a shift of the maximum temperature for styrene content towards higher values for copolymer containing 32.7 wt% PS. In mixtures containing a small amount of PS some isolation of polystyrene chains can occur with the possible formation of microdomains[14]. Because of the presence of such microdomains the probability of molecular interactions between different chains is decreased and results in a shift of the maximum of styrene yield towards higher temperatures. For copolymer with higher PS content one can observe better miscibility and an increase of probability of molecular interactions.



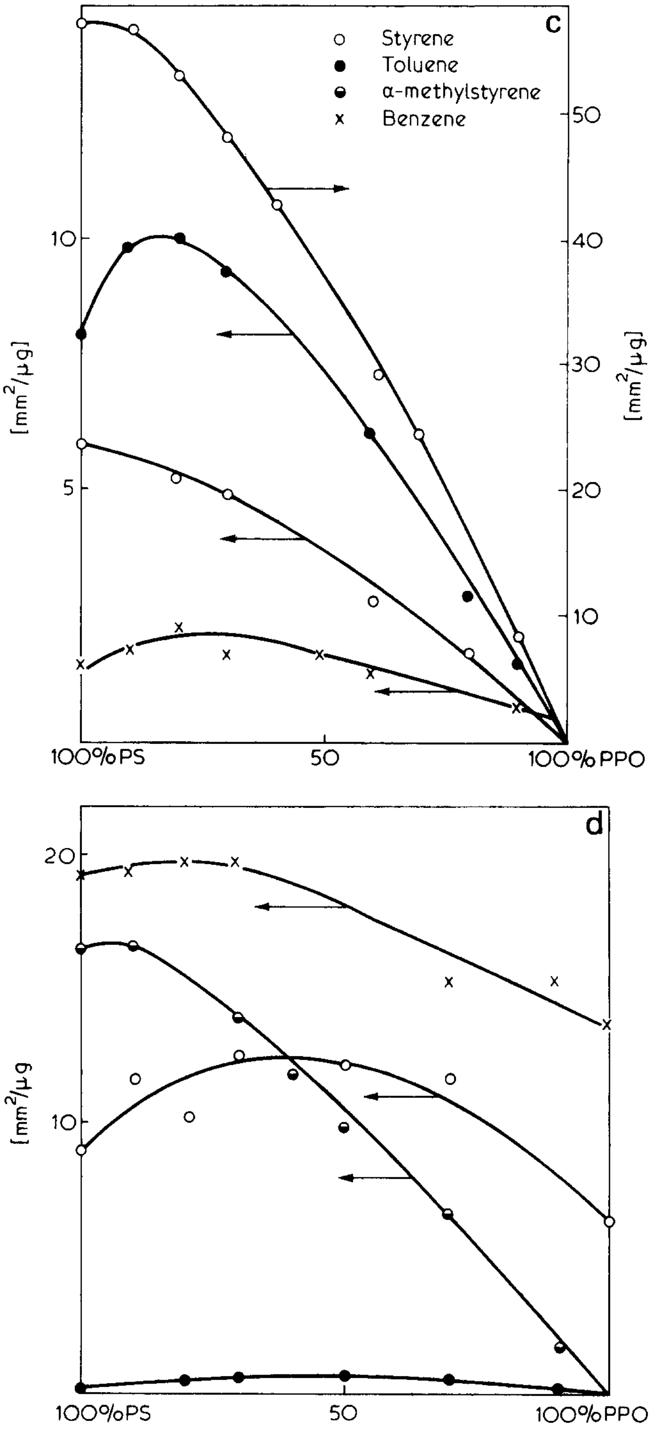


Figure 3 **Dependence of the yield of some pyrolysis products for PS–PPO mixtures on the PPO content (a), 350°C; (b), 450°C; (c), 500°C; (d) 650°C**

The results of our studies of pyrolysis of the PS–PPO mixtures and copolymers lead to the following conclusions:

(1) In a mixture of polystyrene with PPO, polystyrene undergoes mainly depolymerization.

(2) The increase in probability of depolymerization must be caused by a restriction in intramolecular hydrogen transfer, since this process would result in the formation of other scission products.

(3) These limitations of intramolecular hydrogen transfer may result from the close packing of the chains of different polymer in this miscible system.

(4) The relative contributions of competitive processes, i.e. depolymerization, intra- and intermolecular transfer depend not only on the composition of a mixture but also on the temperature. The influence of PPO on the thermal degradation of polystyrene below 400°C is of a stabilizing character such that reduced amount of gaseous products of pyrolysis of the mixture was observed.

(5) The results indicate the greater sensitivity of pyrolytic methods of polymer investigations to interphase diffusion. They also seem to prove that these methods can be applied to the investigation of miscibility of polymeric systems at the molecular level.

The studies of the application of p.g.c. to analysis of the composition of mixtures and copolymers of polystyrene with PPO have shown that at each of the pyrolysis temperatures the dependence of styrene yield on composition deviated from additivity and could be described by the second order regression equation in the following way:

$$Y = a + bx + cx^2 \tag{2}$$

where: Y is the yield of styrene per unit mass of the sample (mm^2/μg); x is the PPO fraction in the mixture; and a is the yield of styrene in the products of PS pyrolysis at a given temperature.

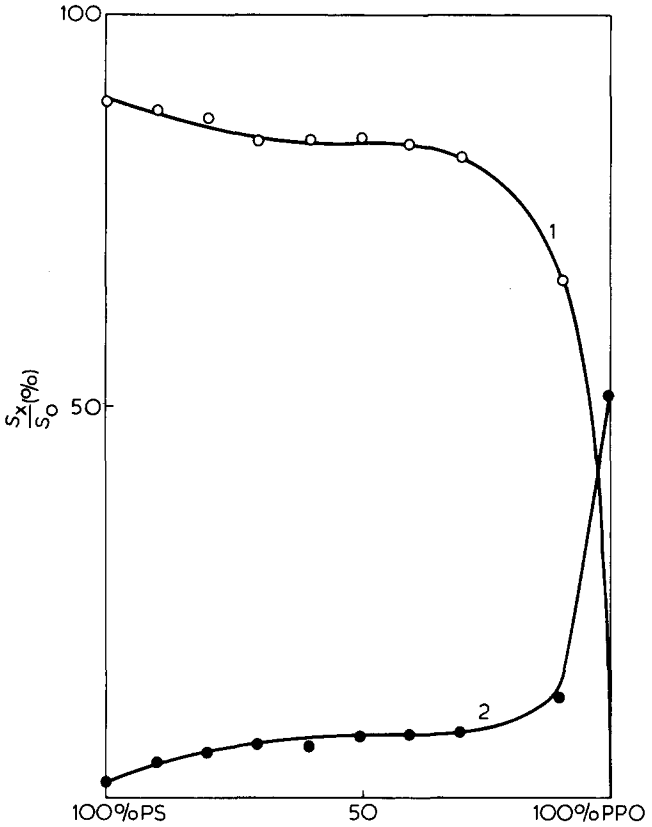


Figure 4 Dependence of relative contributions of styrene (1, —O—) and toluene (2, —●—) in gaseous products of PS–PPO mixture pyrolysis (S_x/S_0) %. Pyrolysis temperature 500°C

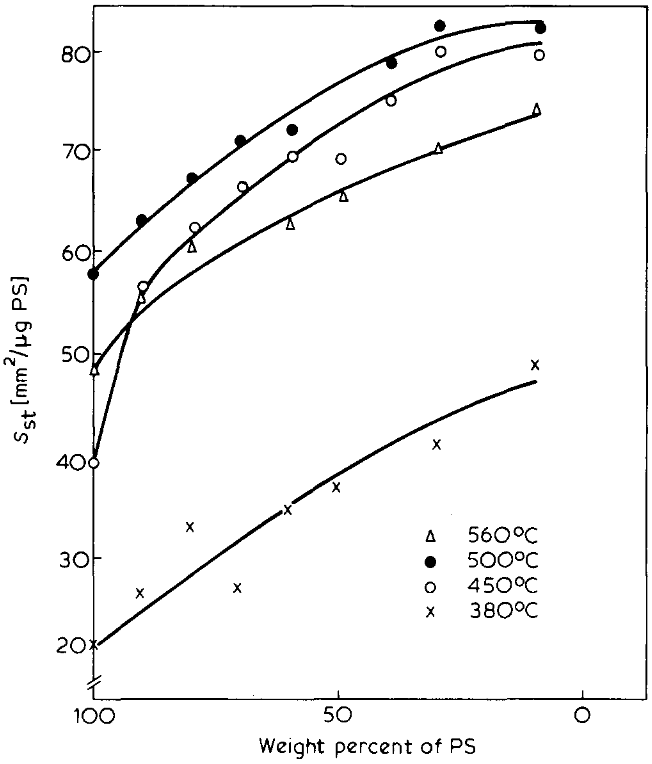


Figure 5 Dependence of the styrene yield S_{st}(mm^2/μg PS) in PS–PPO mixtures on the weight contribution of components

Table 2 Styrene yield S_{st} (mm^2/μg PS) as a function of PS–PPO mixture composition and pyrolysis temperature

Weight percentage of PS	350°C	380°C	450°C	480°C	500°C	560°C	650°C
100	15.7	20.9	39.6	49.9	57.6	48.1	16.9
Mixtures							
90	–	26.3	56.7	–	63.8	55.4	18.8
80	7.4	32.9	62.1	65.3	67.0	60.7	18.6
70	0.3	26.6	66.2	63.3	70.7	55.8	19.9
60	0.2	34.3	69.4	67.4	71.7	63.1	19.8
50	0.1	37.0	69.1	62.6	–	66.7	19.8
40	0.3	–	75.3	74.5	74.6	–	–
30	0.4	41.3	80.4	79.0	83.4	70.8	23.0
10	0.6	59.0	80.3	–	82.7	74.8	26.6
Copolymers							
32.7	–	18.8	67.2	77.0	88.5	91.5	55.6
64.4	–	35.7	63.6	63.4	66.4	55.9	20.5

Table 3 Percentage of styrene in contents of gaseous products (S_{st}/S_0) % as a function of PS–PPO mixture composition and pyrolysis temperature

Wt % of PS	350°C	380°C	450°C	500°C	560°C	650°C
100	64.0	77.7	97.8	89.9	87.1	73.5
90	–	24.3	92.7	86.4	78.5	66.5
80	–	32.8	89.2	87.5	80.7	71.4
60	16.8	21.2	86.3	83.2	–	65.9
50	15.9	20.4	84.6	84.8	75.6	63.5
30	24.6	22.0	81.9	83.2	75.2	57.3
10	10.9	18.2	76.0	66.5	65.7	38.7

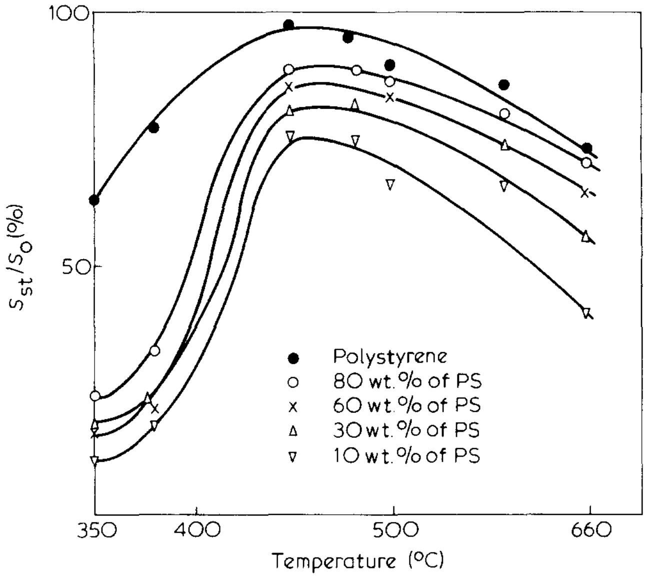


Figure 6 Dependence of styrene percentage in total content of gaseous products (S_{st}/S_0) %, in PS–PPO mixture pyrolysis, on the temperature

The physical significance of parameters b and c is rather difficult to define but they are dependent on the temperature, on the degradation process and microstructure of mixtures and copolymers.

On the basis of the data from *Table 2*, regression equations of the dependence of styrene yield on the composition of the mixture were determined at each of the temperatures. They are as follows:

$$
\begin{aligned}
y_{450\,C} &= 42.5 + 28.0\,x - 75.9\,x^2 \\
y_{480\,C} &= 49.9 - 3.4\,x - 50.1\,x^2 \\
y_{500\,C} &= 57.2 - 34.9\,x - 24.4\,x^2 \\
y_{560\,C} &= 50.5 - 21.5\,x - 29.2\,x^2
\end{aligned}
\tag{3}
$$

Based on styrene yield during pyrolysis of grafted copolymers PPO with PS at the same temperatures (*Table 2*) and using the regression equations, we have determined the PS$-(1-x)$ fraction in copolymers.

The data of weight fractions of PS in copolymers obtained by p.g.c. compared with those obtained by n.m.r. are presented in *Table 5*. Given a 5% error for n.m.r. spectroscopy the best agreement of the results is obtained from pyrolysis at 480°C. The dependence of styrene percentage on the content of the gaseous products in the composition of the mixture (see *Table 3*) indicates that the percentage of styrene in the pyrolysis products at 480 C does not depend on the microstructure and interactions in the PS–PPO system. It shows that this temperature is the most appropriate for analytical uses of p.g.c. for PS (or PPO) determination in the mixture or copolymer of these polymers.

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Table 4 Percentage of toluene in contents of gaseous products (S_T/S_0) % as a function of PS–PPO mixture composition and pyrolysis temperature

Wt % of PS	350°C	380°C	450°C	500°C	560°C	650°C
100	22.1	17.9	1.8	3.1	6.3	9.84
90	–	57.6	3.8	5.3	11.9	12.3
80	–	57.4	5.2	5.9	7.7	12.2
60	76.3	72.2	7.1	7.6	–	12.2
50	69.5	60.9	6.9	6.9	9.4	12.4
30	67.7	63.6	6.6	7.5	9.2	12.8
10	76.7	67.1	12.5	13.4	11.1	13.8
100% PPO	77.5	75.5	72.7	51.3	33.9	17.9

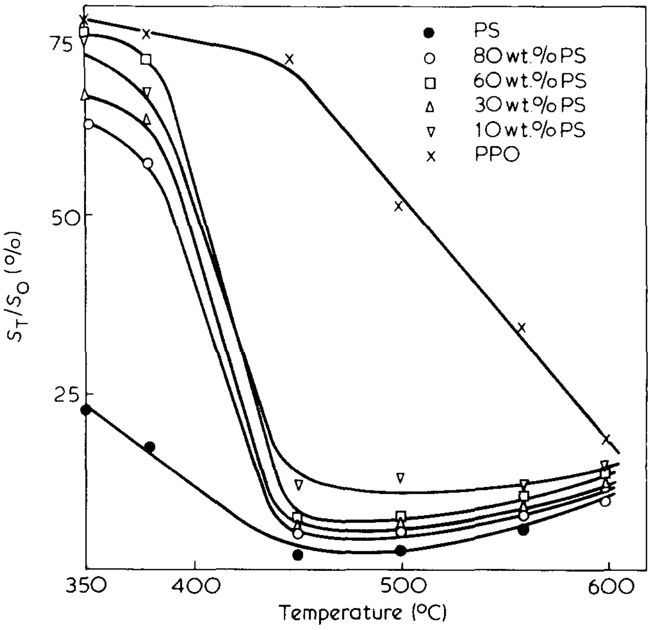

Figure 7 Dependence of toluene percentage in a total contents of gaseous products (S_t/S_0) % in PS–PPO mixture

Table 5 Comparison between PS weight percent in grafted copolymers PS–PPO obtained by n.m.r. and p.g.c.

	p.g.c.			
n.m.r.	450°C	480°C	500°C	560°C
32.7 ± 1.6	26.5	33.5	40.0	48.0
64.4 ± 3.2	59.7	61.7	62.0	58.0
84.8 ± 8.2	84.0	85.0	88.0	88.0

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