Charring Processes in Thermoplastic Polymers: Effect of Condensed Phase Oxidation on the Formation of Chars in Pure Polymers

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Synopsis

Fifteen different pure polymers were studied by thermal methods under air, nitrogen, and nitrous oxide in order to determine their tendency to char in relation with their structure and the experimental conditions used. Styrene polymers and aliphatic polyolefines give chars under air and total volatilization without carbonization under nitrogen and nitrous oxide, showing the essential part played by oxygen in the charring process. On the opposite, ambient oxygen has some effect on the carbonization of polymers containing aromatic rings in their main chain. A schematic mechanism of the charring process is discussed in which condensed phase oxidation, formation of olefinic bonds and crosslinking, dehydrogenation–aromatization are postulated.

INTRODUCTION

Charring processes play an important part in the combustion of polymers, particularly in the case of thermoplastics which form an adherent unbroken char layer during combustion. However, literature data in this field[1-3] do not make it possible to asses the tendency of pure polymers to char because most studies deal with materials containing fire retardants. Moreover, most experiments used in these studies, namely thermal analysis, are carried out under experimental conditions which are very different from those used in combustion studies, particularly with respect to the ambient gas used.

Thus, Camino and Costa have extensively studied the polypropylene/chlorinated paraffin mixtures.[4-10] Almost all the experiments were carried out under nitrogen atmosphere. The authors have shown that the carbonaceous residues formed result from the degradation of the chlorinated paraffin. One study was performed, by these authors, under air[11] with mixtures of chloroparaffin with polyethylene (PE), polypropylene (PP), and polystyrene (PS). In these three cases the presence of the fire retardant which chars masked a possible carbonization process involving the polymer itself.

According to Bakos et al.,[12] the chars formed by thermal degradation under air of the PP/Dechloran 25 and PP/Dechloran 602 mixtures (these dechlorans are Diels-alder adducts of hexachlorocyclopentadiene with cycloocta-1,5-diene and furan, respectively) is due to the decomposition of the dechlorans. In the case of PS, Mackay[3] has shown that this polymer does not char under nitrogen. Its volatilization is quantitative and monomer and few amounts of dimer and trimer are formed. The mechanism of the thermal degradation of the PS was recently reviewed.[10] Taking into account the experimental data, a

mechanism involving competition between unzipping and intramolecular hydrogen transfer depending on the molecular weight of the polymer has been proposed.

The preferential use of nitrogen as ambient gas in most of the thermal analysis studies may be explained by the fact that most authors consider the combustion process as resulting from the thermal degradation of the polymer, the heat required to sustain the endothermic decomposition being supplied by the flame itself. This assumption is not confirmed in the case of PP by Stuetz and co-workers.[13] According to these authors, the nature of the gaseous flammable products supplied by the polymer and the thermal energy necessary for volatilization result essentially from the condensed phase oxidation of the polymer. It has been shown elsewhere[14] that the behavior of PE in air is similar. However, in the case of poly(ethylene terephthalate), Granzow[15] assumes that oxidative degradation does not play any significant part in the volatilization process of this polymer.

While it is now generally accepted that condensed phase oxidation plays a prominent part in the volatilization process of a number of polymers, studies on a possible role of this oxidation in the charring process of pure polymer have received little attention. Two papers seem to be of interest from this point of view. Kishore and Mohandas[16] have shown that PS-containing ammonium phosphates chars when TGA experiments are carried out under oxygen whereas total volatilization without carbonization is observed if nitrogen atmosphere is used. However, it is well known that ammonium phosphates promote charring in polymers. On the other hand, Clark[17] has observed that, when PS is ignited by a small hydrogen flame, a superficial layer of carbon is formed on the polymer at the contact of the ignition flame. This phenomenon is not observed with poly(methyl methacrylate).[18]

The aim of the present work is to study by thermal methods the relationships between the chemical structure of a polymer and its ability to char. As indicated above, the oxidation process seems to play an important part in this process; thus we studied more precisely the effect of oxidation conditions on the importance of the charring process. For that reason, particular attention was devoted to the study of the effect of nitrous oxide on the degradation behavior of the materials studied. Indeed, many authors (see particularly Refs. 15 and 19) have compared the oxygen index (OI) and the nitrous oxide index (NOI) to find out whether a fire retardant acts in the gas phase (OI and NOI vary differently as the concentration of the fire retardant increases) or in the condensed phase (the variation of the indices is then similar). As noticed by Granzow and Cannelongo,[20] this hypothesis implies that both oxygen and nitrous oxide are without any effect on the polymer degradation and it was of interest to check that assumption.

EXPERIMENTAL

Materials and Products

The polymers used in this investigation are listed on Table I. All the materials which were obtained from a variety of sources were used as received without further treatment. Poly(2-vinylpyridine)[21] and poly(α-methyl-styrene)[22] were prepared by anionic polymerization. Polynorbornene was

TABLE I
Materials Studied

Polymer	Trade name	Abbreviations used	Source
Low density polyethylene	—	PE	CdF Chimie S.A.
Polypropylene	KM 6100	PP	Shell (Doneco S.A.)[a]
Polybutene	—	PBut	CdF Chimie S.A.
Polybutadiene	45 M	PB	Arco[b]
Polynorbornene	—	PNor	LRM Paris
Poly(2-vinylpyridine)	—	P2-VP	LRM Paris
Polystyrene	—	PS	CdF Chimie S.A.
High impact polystyrene	Lacqrene 6631	—	Atochem S.A. (Doneco S.A.)
Styrene—acrylonitrile copolymer	Lustran 31	SAN	Monsanto (Doneco S.A.)
Acrylonitrile–butadiene–styrene copolymer	Dow 213	ABS	Dow Chem. (Doneco S.A.)
Polybutyleneterephtalate	Orgater TMNO	PBTP	Atochem S.A. (Doneco S.A.)
Modified poly(phenylene oxide)	Noryl 731-802	PPO/PS	General Electric (Doneco S.A.)
Polysulfones	1700	PPSU	Amoco (Doneco S.A.)
Poly(α-methylstyrene)	—	PMeSt	LRM Paris

[a] We thank Doneco S.A. for the supply of these products and financial support.

[b] Furnished by LRM Paris (Laboratoire de Recherche sur les Macromolecules, Universite Paris-Nord).

prepared by metathesis.[23] For comparative study, we have used carbon "Darco" from Atlas Powder Company. A high purity grade nitrous oxide from "Air Liquide S.A." containing less than 10 ppm of oxygen was used. Styrene–divinylbenzene copolymer, a mixture of freshly distilled styrene (10 g) and divinylbenzene (4 g), was heated at 80°C for 4 h in presence of benzoyl peroxide (0.1 g) in a glass tube. The sample obtained may be used for combustion experiments or ground for thermal analysis studies.

Apparatus and Procedures

All our experiments were carried out by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) using the Stanton Redcroft analyzers DTA 673-4 and TG 750/770, respectively. Flowing air, nitrous oxide, nitrogen, or mixtures of them were used in all cases (DTA: 100 cm^3/min, TGA: 50 cm^3/min); careful purging was carried out in the case of nitrous oxide, nitrogen and mixtures. A cylindrical platinum crucible (diameter: 6.3 mm; height: 8.3 mm) was used as a sample holder in the DTA experiments and a platinum crucible of complex shape was used in TGA. The samples (25 mg in DTA, 5 mg in TGA) were applied in form of powder or of small chips according to the polymer concerned. Heating rates between 5 and 20°C/min for DTA and between 5 (in one case 2°C) and 100°C for TGA were used. At the beginning of the experimental work, the measurements were repeated in order to check reproducibility of the analysis. They were found to be satisfactory.
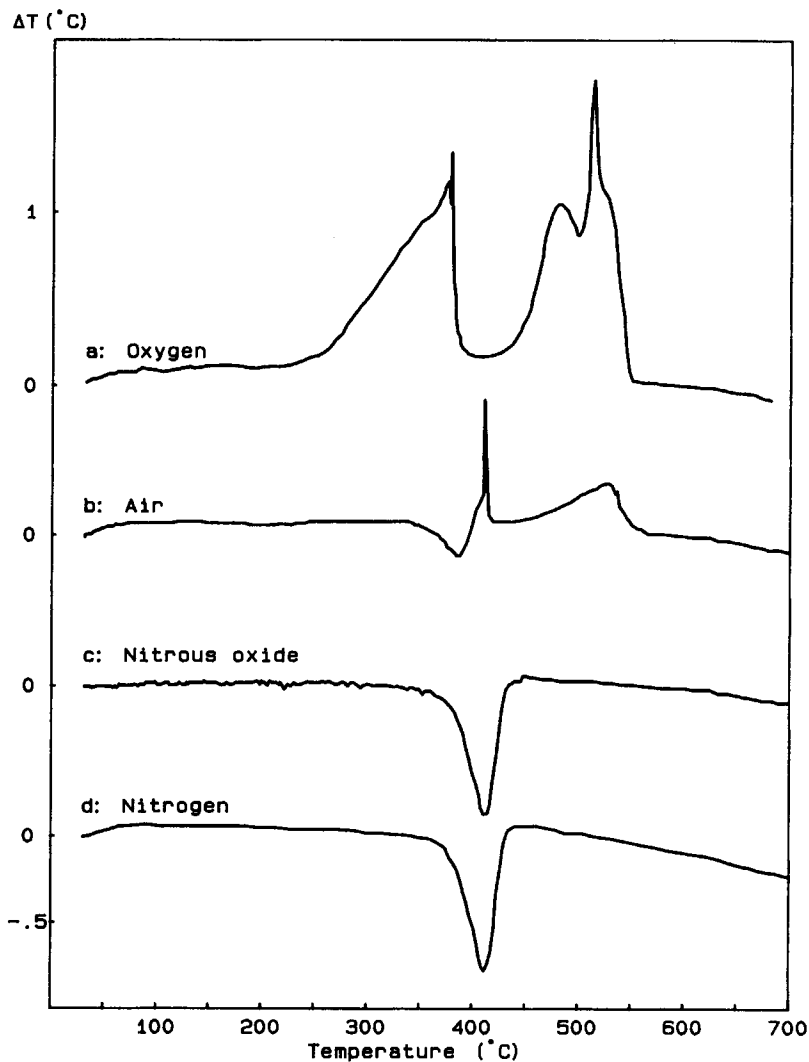
ΔT (°C)

Fig. 1.   Effect of the nature of ambient gas on the DTA curves of polystyrene (heating rate: 5°C/min.).

RESULTS AND DISCUSSION

Polystyrene

According to the results already mentioned, the degradation of PS under nitrogen leads to a quantitative volatilization of the polymer. The DTA curve of PS under nitrogen [Fig. 1(d)] shows a single endothermic peak corresponding to the carbon—carbon bond scission with formation of monomer mainly. Under air the DTA thermogram presents more complex features [Fig. 1(b)]. Apart from the endothermic peak, we observe at about 410 and 530°C two exothermic peaks corresponding to a charring process associated with the condensed phase oxidation of the polymer as shown below.

If a DTA experiment, carried out according to the procedure already described (see Experimental), is interrupted at about 400–420°C and the crucible quickly cooled, a black carbonaceous residue is obtained corresponding to 10% of the initial weight of the sample. Heated under air, this residue gives a strong oxidation peak by DTA at 530°C, but this residue is not volatilized under nitrogen. A DTA experiment carried out under air with the superficial black layer of char formed by combustion of a rod of PS in an oxygen index apparatus gives mainly the same exothermic peak at 500–550°C, showing that the charring processes taking place in the DTA and in a combustion experiment are of the same kind. At last, DTA experiments carried out under air with a variety of carbons of different sources have shown that their oxidation seems to occur between 400 and 700°C according to their purity. From all these results, we may deduce that the DTA exothermic peak observed at 530°C is characteristic of the oxidation of chars formed in an earlier phase of the oxidative degradation process. We will discuss, further, a possible interpretation of the exothermal process taking place at 410°C.

As expected from these observations, charring may be more important if the DTA experiment is carried out under pure oxygen. The DTA curve of Figure 1(a), in which a strong peak in the range 500–550°C is observed, confirms this assumption. Finally, it was of interest to compare these results with those obtained under the mild oxidant nitrous oxide. Surprisingly, as shown in Figure 1(c), the behavior of this gas is similar to that of the inert gas nitrogen. This difference in the behavior of these two oxidants is of significant importance. Indeed, it leads us to question the interpretations generally proposed from comparative studies of OI and NOI, all these interpretations being supported by the assumption that the condensed phase oxidation does not play any part in the combustion process in these two gases.

The results obtained from TGA experiment confirm the data from DTA. As expected, two main steps are observed in the TGA curves under oxidizing atmosphere [Figs. 2(a) and (b)], the second corresponding to the oxidation of chars. These curves enable us to evaluate the amount of chars formed (respectively 15, 6, and 0% under pure oxygen, air, and nitrogen). The curve obtained under nitrous oxide—not shown here—is superposed to that obtained under nitrogen.

At this stage of our work, it was of interest to study the effect of the concentration of oxygen in a nitrogen/oxygen mixture, on the degradation of the polymer and particularly on the formation of chars. The DTA curves obtained with 18, 16, and 14% of oxygen are represented in Figure 3 (b,c, and d respectively) and compared with those obtained in air [21% of oxygen: Fig. 3(a)] and in nitrogen [0% of oxygen: Fig. 3(e)]. From these results, we may conclude that the charring process is strongly dependent on the oxygen concentration in the case of PS. Figure 3 shows that significant char formation appeared above 18% of oxygen, a value similar to that of oxygen index of PS ($\approx 18.5\%$). We have seen above that, according to studies of Clark, ignition of PS is associated with superficial char formation at the flame–polymer interface. Our results seem to show that charring processes are, in fact, associated —at least in the case of PS—with the overall combustion process. Moreover, we observe that the oxygen concentration used has little effect on the narrow exothermic peak at about 410°C. It seems possible to assume that some steps
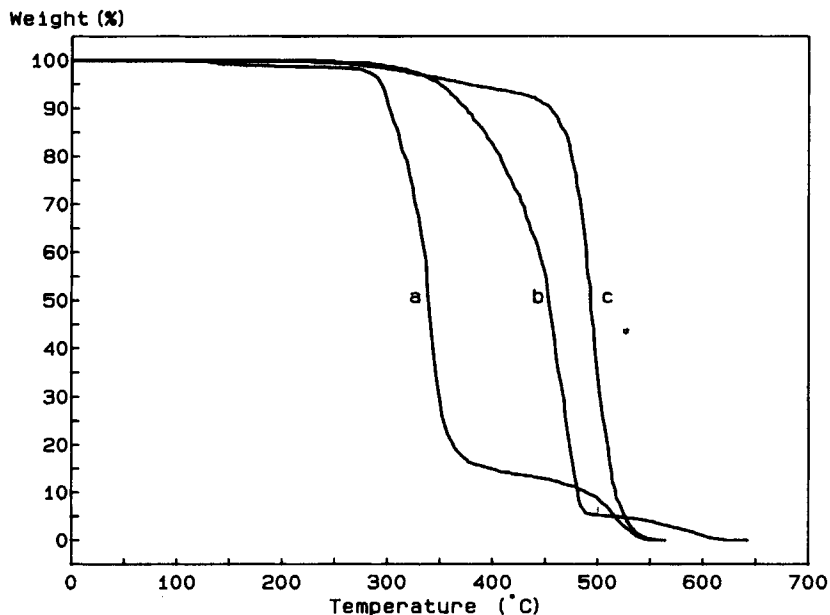
Fig. 2.   Effect of oxygen (a), air (b), and nitrogen (c) on the TGA curves of polystyrene (heating rate: 5°C/min.).

of the overall process of carbonization, as that reaction occurring at 410°C, are less sensitive to oxygen than other steps.

These results differ strongly from those of Stuetz et al.[13] concerning PP. In the case of this polymer Stuetz et al. showed that condensed phase oxidation occurs at a percentage of oxygen as low as 1%. Our results show the lower sensitivity of PS to oxidation compared with PP. Except in the case of the curve e, the DTA curves of Figure 3 were obtained with a programmed heating rate of 10°C/min. The differences observed according to the oxygen concentration at this rate are not observed with a heating rate of 5°C/min. In this last case, charring occurs until the concentration of oxygen reaches 10%. This result is not surprising. Since the condensed phase oxidation plays an essential part in the charring process, this heterogeneous phase reaction being dependent on the diffusion rate of the oxygen into the solid or melted polymer, we may suppose that the heating rate used in the DTA or TGA experiment will influence the amount of chars formed by oxidative degradation. The DTA curves of Figure 4 and the data tabulated on Table II confirm this hypothesis.

From the curves of the Figure 4, it seem possible to conclude that the extent of the charring process is dependent on the competition between two reactions: the endothermic scission of the carbon—carbon bonds with formation of monomer which promote volatilization and, at about the same temperature, an exothermic process which leads to the formation of a precursor of the chars. We see from Figure 4 that, when the heating rate is reduced, the exothermic peak at 400–450°C is strongly shifted toward a lower temperature whereas the maximum of the endothermic peak is not changed. The result is a decrease of the volatilization process in favor of the charring process. Accord-
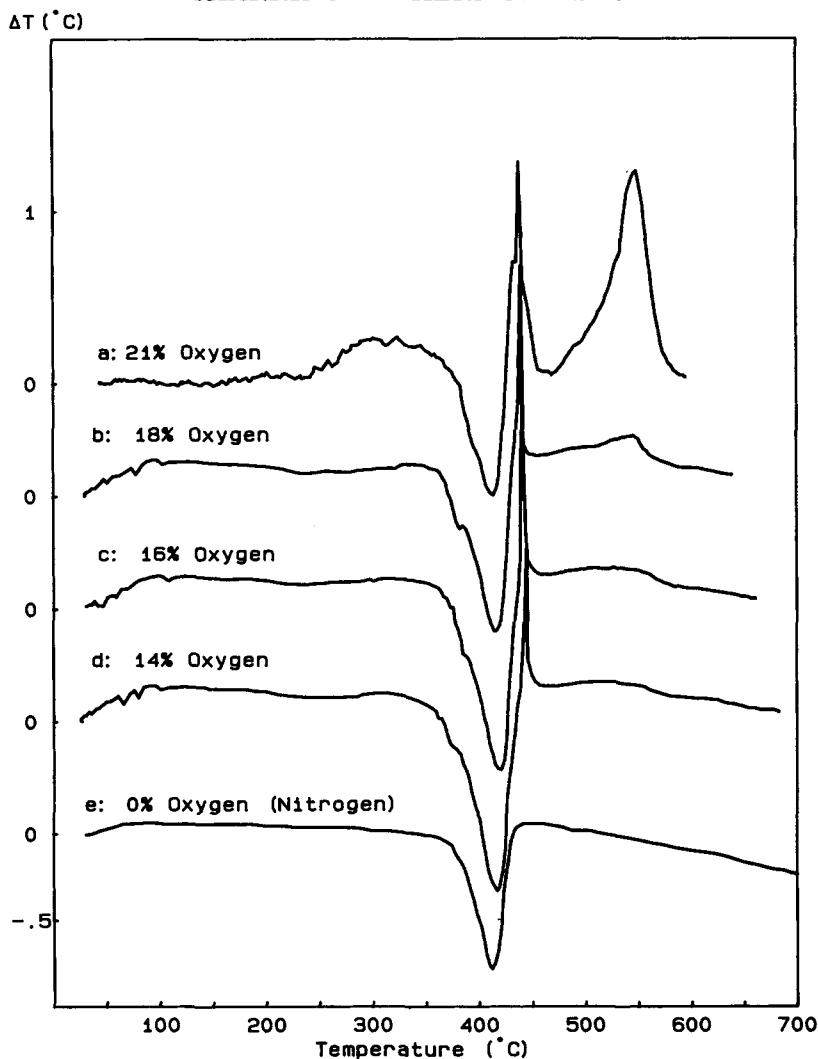
ΔT (°C)

Fig. 3. Effect of oxygen concentration on the DTA curves of polystyrene (heating rate: 10°C/min.).

ing to the work of Kishore and Mohandas,[16] already mentioned, chars result from the formation and the subsequent transformation of olefinic bonds in the polymer chain. These double bonds should be formed by thermal degradation of phosphoric esters resulting from the interaction between ammonium phosphates used by this author as fire retardants and the polymer. Moreover, these authors have emphasized the role of transient peroxides in the formation of phosphoric esters. In the case of pure PS this mechanism cannot be proposed. However, Costa and Camino[10] have shown that, in the presence of chlorinated paraffin, PS gives relatively important amounts of oligomers containing conjugated olefinic bonds. The authors attribute the formation of these compounds to the interaction of chlorine radicals with the polymer. We assume that, under oxidative conditions, oxygen may play a similar role. In order to propose a more accurate mechanism of the charring process, we will now describe the behavior of other polymers.
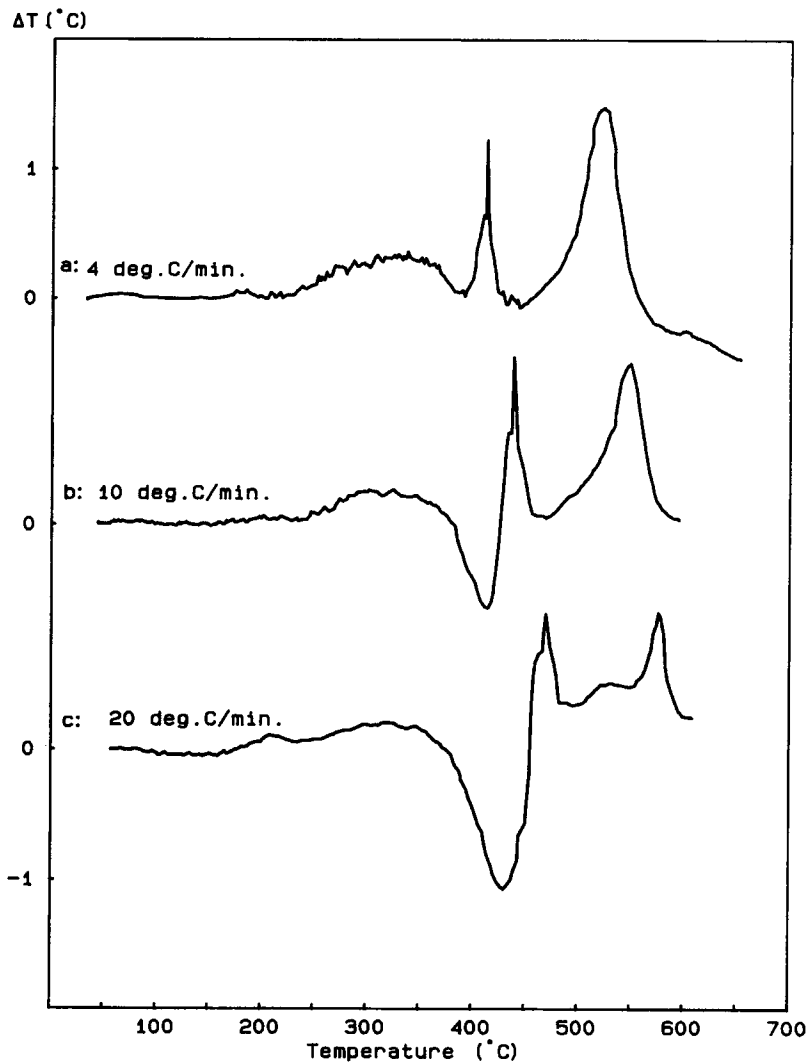
ΔT (°C)

Fig. 4.   Effect of heating rate on the DTA curves of polystyrene.

TABLE II
Amounts of Chars (%) from TGA at Various Heating Rates: Polystyrene

Heating rate (deg/min)	2	5	10	20	50	100
Pure PS	9	6.5	5	3	.5	0
High impact PS	—	7.5	5	3	2.5	2

Other Polymers

As shown above, an oxidizable polymer, an unsaturated bond forming polymer, and a material containing reactive benzylic carbon—hydrogen bonds may present a strong ability to char. Conversely, a styrene polymer in which the benzylic bond is blocked could not char.

TABLE III
Amounts of Chars (%) from TGA Experiments at Various Heating Rates: Polystyrene Analogs and Unsaturated Polymers

Rate (deg/min) (ambient gas)	5 (air)	10 (air)	20 (air)	50 (air)	100 (air)	10 (nitrogen)	5 (nitrous oxide)
PMeSt	0	—	—	—	—	—	—
P2-VP	33	29	26	21	16	2	2
PB	25	15	—	4.5	—	2	2
PNor	23	12.5	—	4	—	2.5	2
P(S–DVB)	22	19	—	—	11	2.5	2.5

The data tabulated in Table III concerning poly(α-methylstyrene) (PMeSt), poly(2-vinylpyridine) (P2-VP), polybutadiene (PB), and polynorbornene (PNor) confirm our assumptions (the results concerning styrene–divinylbenzene copolymer—P(S–DVB)—will be discussed later). With exception of the first case, the polymers strongly char. These results allow a further discussion of a possible mechanism of the charring process. The first two results of Table III show that the benzylic carbon—hydrogen bonds play an important part in the carbonization process. We may suppose that a more reactive benzylic bond may lead to a higher unsaturation in the polymer chain. Indeed, it is known that the benzylic bond of isopropylpyridine is more reactive than that of isopropylbenzene.[24] Similar relative reactivities might be present in the case of P2-VP and PS, respectively. The charring behavior observed for these two polymers is then consistent.

If unsaturation plays a key part in the carbonization it is not surprising to obtain important amounts of chars by degradation of PB and PNor as shown in Table III. For the role played by the olefinic bonds, we may propose two possible explanations, taking PB as an example. First, it is well known that PB, in acidic medium, gives intramolecular cyclization, leading to condensed polycyclic structures.[25, 26] Such a reaction might occur under thermal conditions through intermediate radicals. The polycyclic intermediates formed may then lead, by aromatization, to char precursors. If such a mechanism is involved, PNor in which cycles are included must char more profusely than PB. This is not the case, and it seems more likely that the olefinic bonds allow crosslinking reactions leading to a three-dimensional structure which is a good precursor of char as shown by the results obtained in the case of the styrene–divinylbenzene copolymer (Table III). The DTA curves obtained with PB [Figs. 5(a),(b) and (c)] and with PNor (not represented here) support this second hypothesis. We see that, independently of the ambient gas used, PB gives an exothermic reaction at 350°C (400°C in the case of PNor) which may be attributed to a crosslinking reaction. To confirm this assumption, we have carried out a DTA experiment under nitrogen, the sample of PB which is liquid being introduced in a quartz DTA crucible sealed under nitrogen. The experiment is stopped at 400°C just after the occurrence of the exotherm. After cooling, the crucible contains a light yellow solid insoluble in toluene (in which PB is soluble); moreover, this solid decomposes by heating without melting.

As in the case of PS, oxidation conditions have an important effect on the amount of carbonization products. However, slight amounts of chars are
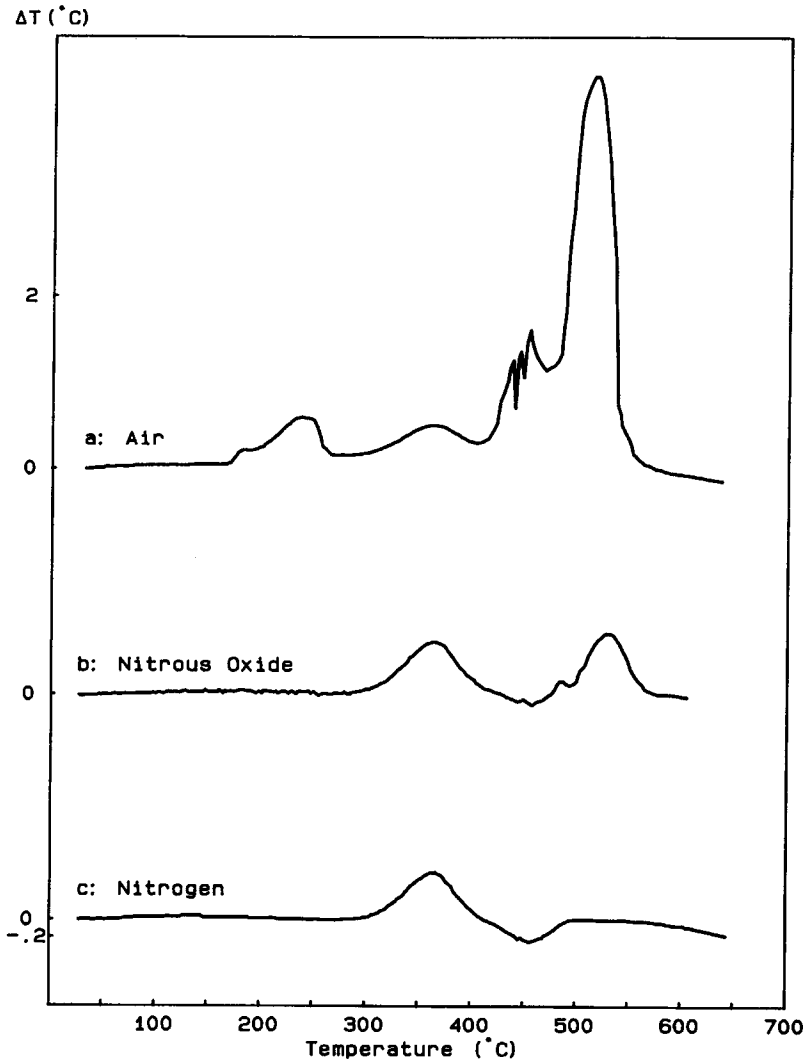
ΔT (°C)

Fig. 5.   DTA curves of polybutadiene under various ambient gases (heating rate: 5°C/min.).

formed under nitrogen. We think that a slight oxidation of these polymers at ambient temperature during storage may explain this result. Nitrous oxide has no effect on the charring process, and the results (Table III) are the same as under nitrogen. In the case of nitrous oxide, however, we observe either by DTA [Fig. 5(b)] as well as by TGA an oxidation of the carbonaceous residue occurring at a higher temperature than under air. This result is confirmed by DTA experiments carried out on samples of pure carbon as shown on Figure 6. It is rather surprising to observe different behaviors between the polymers already studied and the elemental carbon with nitrous oxide. A possible explanation of this fact is that, at temperature higher than 585°C, at which carbon is oxidized, nitrous oxide is partially decomposed in oxygen and nitrogen at an appreciable rate.[27] The oxidant should be oxygen and not

ΔT (°C)

.5

a: Air

0

b: Nitrous oxide

0

-.3

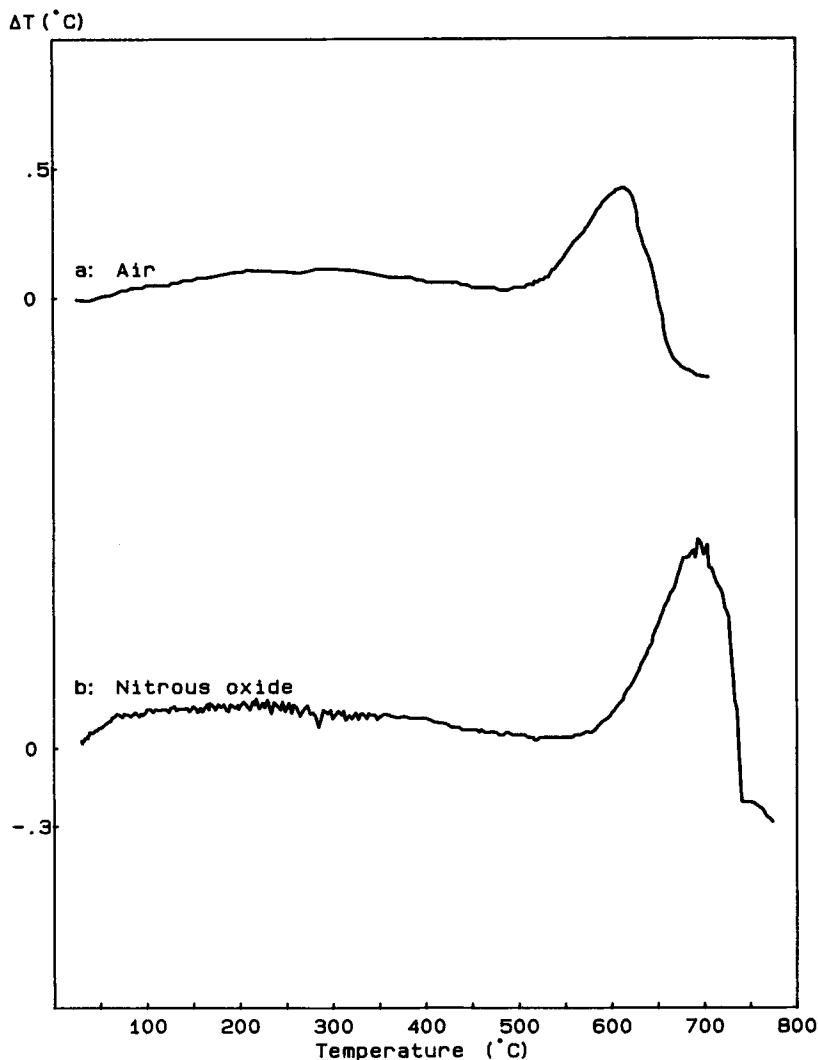100 200 300 400 500 600 700 800
Temperature (°C)

Fig. 6. DTA curves of carbon "DARCO" under air and nitrous oxide (heating rate: 5°C/min.).

nitrous oxide. At temperatures lower than 585°C, nitrous oxide itself should be too mild an oxidant to react with polymers.

To confirm the importance of oxidability of the material to the extent of the charring tendency of the polymer, we studied two other classes of materials: styrene–acrylonitrile (SAN) copolymer and acrylonitrile–butadiene–styrene (ABS) copolymer, which both contain the electro-attracting nitrile group. This group facilitates condensed oxidation of the polymer chain.[28] In the second class we studied polyethylene (PE) and polypropylene (PP), which present a strong ability to condensed phase oxidation as shown above, and the closely related polymer polybutene (PBut). The results are shown in Table IV. In these cases too, oxygen plays an essential part in the formation of chars. Although SAN and ABS show a strong tendency to cyclize[29] under nitrogen, no chars are formed when thermal analysis is carried

TABLE IV
Amounts of Chars (%) from TGA at Various Heating Rates: Styrene Copolymers
and Aliphatic Polyolefines

Rate (deg/min) (ambient gas)	5 (air)	10 (air)	20 (air)	50 (air)	100 (air)	10 (nitrogen)	5 (nitrous oxide)
SAN	16	11	7.5	4	2.5	0	0
ABS	15	11.5	8.5	5.5	5	0	0
PE	—	13	—	7	—	0	0
PP	8.5	7	5.5	3.5	1	0	0
PBut	—	10	—	3	—	0	0

out with an inert ambient gas. In the case of PE, PP, and PBut, the results are not in good agreement with their tendency to peroxidation. Indeed, it is well known that PP gives peroxides about 100 times faster than PE. However, it is PE which chars more abundantly. According to Costa and Camino,[8] PE shows a strong tendency to crosslinking reactions in the presence of chlorinated paraffin. These reactions are due to Cl radicals. As we have already assumed in the case of PS, oxygen may act in a similar way as chlorine radicals giving secondary carbon radicals by interaction with the polymer chain. These carbon radicals should recombine by crosslinking. This reaction promotes chars, as already discussed.

All our results suggest that crosslinked or polycyclic structures must be formed as precursors of carbonaceous residues. A last step, in this transformation of the precursors into chars, should be a dehydrogenation reaction leading to carbonization products through polyaromatic intermediates. The well-known charring tendency of the polymers containing aromatic rings in their main chain[1] confirms this assumption. The effect of oxygen on the amounts of carbonization products formed has not yet been investigated. Table V contains the experimental data we have obtained in this case compared with some data from literature. The polymers studied were poly(butylene terephthalate) (PBTP), PS/polyphenylene oxide blends (PPO/PS), and poly(phenylene sulfone) (PPSU). Two values are given when the TGA experiments are performed under nitrogen. They correspond to the sudden change of the slope of the weight vs. temperature curve and the percentage of residue stable at 900°C under nitrogen, respectively. Figure 7 represents as an example the TGA curves obtained with PBTP respectively under air and nitrogen. We see that the effect of oxygen on these three polymers is lower than in other cases. We confirm here the hypothesis of

TABLE V
Amounts of Chars (%) from TGA Experiments at Various Heating Rates: Aromatic Polymers

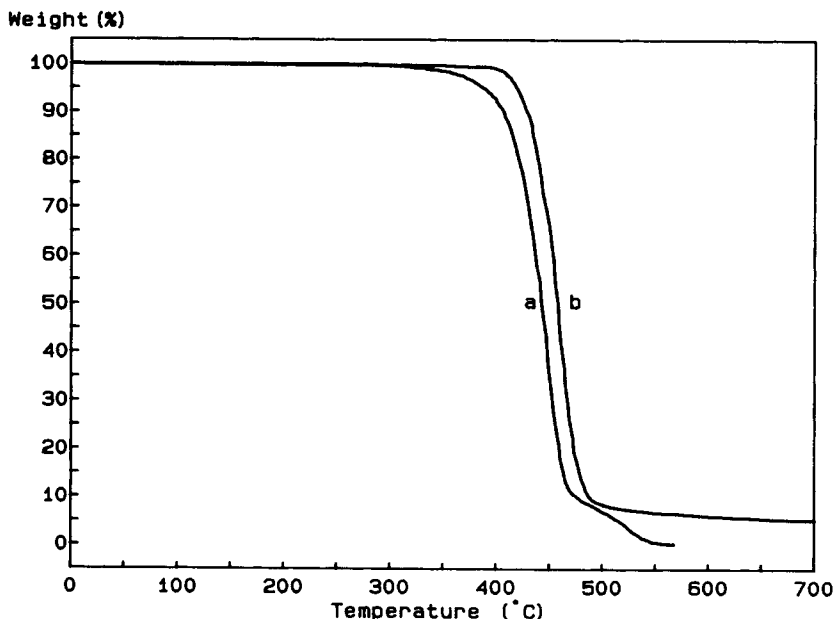| Rate (deg/min) (ambient gas)	5 (air)	10 (air)	20 (air)	50 (air)	100 (air)	10 (nitrogen)	50 (nitrogen)	Ref. 3 (nitrogen)
PBTP	13	11	12	12	11	9–5	8–6	—
PPO/PS	33	33	32.5	26.5	19.5	18–12	17–10	40.4 (pure PPO)
PPSU	57	50	47.5	46	?	42–37	39–33	48

Weight (%)

Fig. 7. TGA curves of poly(butylene terephtalate) under air (a) and nitrogen (b) (heating rate: 5°C/min.).

Granzow and Cannelongo[20] already cited, concerning the insensivity of poly(ethylene terephthalate) toward condensed phase oxidation. It seems that oxygen has a very small effect on the last step of the charring process, namely, the transformation of aromatic structures into chars. However, this smaller effect of ambient oxygen may be due to the presence of functional oxygen in these polymers.

CONCLUSIONS

All the polymers studied in this paper generate chars by thermal degradation. Oxygen has a decisive effect on the charring process except in the case of polymers containing aromatic rings in their main chain.

The first step of the charring process is the condensed phase oxidation of the polymer probably leading to the formation of olefinic bonds in a second step. In a third step crosslinking and/or cyclization reactions may occur. The interaction between oxygen and the network so formed may lead to carbonaceous residues by dehydrogenation–aromatization. The mild oxidant nitrous oxide has no effect on these transformations, and this result may allow one to reassess the results obtained from NOI experiments.

This study raises two questions: First, have fire-retardant additives any disturbing effect on the oxidation–carbonization process? The next paper will describe the effect of halogen containing fire retardants, the question of the relative importance of the gas phase, and condensed phase effect of these additives being still debated. Secondly, what is the real effect of charring on combustion parameters? Is there any combustion test allowing one to differentiate effects due to the chars from the other inhibiting interactions? Our work in this field is in progress.

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